REACTOR
FUEL
PROCESSING

A Quarterly Technical Progress Review

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY

October 1960

● VOLUME 3

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foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Office of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., A. A. Chilenskas, I. G. Dillon, P. Fineman, J. Fischer, A. A. Jonke, S. Lawroski, W. J. Mecham, W. B. Seefeldt, V. G. Trice, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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contents

COMMERCIAL ASPECTS OF FUEL PROCESSING

Domestic and Foreign Government Processing Programs

In October 1959, AEC's Division of Production sponsored a symposium at Richland, Wash., on chemical processing of irradiated fuels from power, test, and research reactors. The proceedings of this symposium, recently issued, constitute one of the best collections of papers on plans, procedures, and facilities for processing various types of fuel elements by decladding, dissolution, and solvent extraction. Introductory remarks made at this symposium, concerning the scope and objectives of the AEC program of power-reactor fuel processing, were reported in a previous Review.[1] Papers describing the receiving and storage of fuel, mechanical treatment, dissolution, extraction, and waste-treatment processes and facilities at the four sites — Hanford, Idaho Falls, Savannah River, and Oak Ridge — are reviewed in appropriate sections of this issue of *Reactor Fuel Processing*.

At the same symposium, fuel processing in the United Kingdom's civil power program was described by Tuohy, who is the Works General Manager at Windscale and Calder Hall.[2] The British power program calls for 12 nuclear power stations using natural-uranium-fueled graphite-moderated CO_2-cooled reactors. The total output of 5000 to 6000 Mw is to be in operation by 1966. Some irradiated fuel from the power program will become available for chemical processing in 1962, and the quantity available will build up to between 500 and 1000 tons having an irradiation level of 3000 Mwd/ton. To meet this commitment, the United Kingdom Atomic Energy Authority (UKAEA) is designing a new chemical separation plant which is scheduled to be in operation in 1963. Subsequent buildup will necessitate the construction of an additional chemical processing plant for operation in 1966. The existing chemical plant at Windscale has been modified to process all the irradiated fuel from the eight Calder Hall type reactors already in operation. It is likely that the first fuel from the United Kingdom's civil power program will be processed through the existing plant in 1962. The primary separation process used in this plant is solvent extraction with dibutyl carbitol solvent in packed extraction columns. The proposed new plant for 1963 will use tributyl phosphate (TBP)-kerosene solvent (Purex process) and box type mixer-settler contactors. This type of contactor is also used in the United States at the Savannah River Laboratory (see A. W. Joyce et al., Design Versus Performance of Process and Equipment in a Large-Scale Radiochemical Separations Plant, *Nuclear Eng. Sci. Conf., 5th, Cleveland 1959, Preprint V-71*).

The history and program of the Eurochemic Company were described by Detilleux of the Eurochemic Study and Research Office.[3] The company was officially created in July 1959 to serve the needs of 13 member countries in the field of nuclear fuel processing. The Eurochemic Research and Study Office started its work earlier, in April 1958. Present plans call for construction of a chemical processing pilot plant with special emphasis on research and development. The capacity has been fixed at 350 kg/day for various types of fuels from natural up to 5 per cent enrichment. The selected site is at Mol, Belgium, adjoining the Belgian Nuclear Laboratories. The proposed process is Purex type (TBP-hydrocarbon solvent) with pulsed-column contactors and with fuel decladding procedures of the type planned in the United States. The Eurochemic Company laboratories are scheduled for completion at the end of 1962, and the plant is scheduled for completion in 1963. The estimated plant cost is

$20 million, $12 million being invested in the main process building and equipment.

Industrial Participation in Fuel Processing

An AEC decision concerning its future plans for expansion of existing chemical processing facilities to handle spent fuels from privately and publicly owned reactors is awaiting results of a survey it is making of industrial plans to enter the field. The Industrial Reprocessing Group, made up of Davison Chemical Company and five reactor-building utility companies, has nearly completed its study on building a private processing plant. A report to AEC was scheduled[4] for August 1960.

The UKAEA has entered into collaboration and license agreements with two British chemical engineering firms. The agreements are the first of their kind to help British industry compete for export business in the design and manufacture of radioactive chemical processing plants. Personnel of the two companies, W. J. Fraser and Co., Ltd., and Nuclear Chemical Plant, Ltd., have been receiving training from the UKAEA in the design and operation of nuclear chemical plants since 1958. Processes covered in the agreements include the production of uranium metal from ore concentrates and the processing of spent fuel elements. The UKAEA, in return for royalties, offers the companies nonexclusive license on UKAEA patents, training of technical staff, and assistance in commissioning particular plants to be built by the companies.[5]

A thorium-U^{233} fuel-cycle development program is to be undertaken by Allis-Chalmers Manufacturing Company for Italy's Comitato Nazionale per le Ricerche Nucleari. The joint five-year research and development program is intended to demonstrate feasibility and economics of a thorium-U^{233} fuel cycle for power-reactor systems. It will include design, construction, and operation of an integrated pilot plant in Italy for thorium-uranium fuel-element processing and remote fabrication, plus a study to determine the most favorable reactor type for exploitation of developments in thorium technology, leading to conceptual design of a large central-station reactor.[6]

The New York State Office of Atomic Development has announced the selection of Vitro Engineering Company to survey New York State for the purpose of locating one or more sites for the safe storage of radioactive waste products. The Office expressed the hope that this project will help attract to the state a privately sponsored nuclear fuels processing plant.[5]

The Rio Tinto Mining Company of Canada, Ltd., last year joined with Dow Chemical of Canada, Ltd., to extract and process thorium from uranium waste liquors. Rare earths will also be recovered. This thorium plant began production in March 1959, and full-scale production of thorium salts of 100 to 200 tons annually was expected in July 1959. The operation utilizes a solvent-extraction recovery step. Thorium concentrates are now being purchased in the United States at approximately $4.50 per pound.[7]

Radioisotope Production

It has been reported from Great Britain that the substitution of cobalt in control rods in British power reactors will provide a relatively large low-cost supply of Co^{60}. The control rods are left partially inserted in the center of the reactor core as a flux flattening device. Possible price reductions to 70 cents per curie are predicted for large sources.[5]

The UKAEA revealed in June that three 150,000-curie Co^{60} irradiators are expected to be in operation within 18 months. They will be used for sterilization of pharmaceutical and surgical equipment and supplies. The plants will be patterned after the Wantage Research Laboratory pilot irradiator, which has just gone into operation. The UKAEA will make cobalt available to the commercial plants at 70 cents per curie, with specific activity of 1 to 5 curies/g. Irradiation costs in the new facilities will be about $1.50 per package for packages of about 1 cu ft. Estimated construction cost of the plants is $150,000 to $180,000 each.[8]

United Kingdom authorities also disclosed that they are cooling off to the possibility of building a cesium separation plant. Design contracts for a plant of 1-million-curie capacity were let nearly two years ago. But, in view of the availability of Co^{60} used as a flux flattener in the U. K.'s power-reactor program, recovery of cesium is not now considered justifiable.[8]

A contract study was recently completed for the AEC's Office of Isotopes Development to determine the feasibility and economics of radioisotope production in three U. S. power reactors: Dresden, Shippingport, and Piqua. According to the report, all three reactors have the capacity for producing very significant amounts of tritium, C^{14}, and Co^{60}. With the Dresden reactor it would be possible, without significantly interfering with reactor power output, to produce annually about 600,000 curies of Co^{60}, which is 3.2 times the 1959 market. Assuming that this amount could be sold and assuming a 15 per cent profit on sales, the report indicates that it would be possible to lower the selling price of the Co^{60} (specific activity of 18.4 curies/g) from the AEC's current price of $3.10 per curie to $0.47 per curie.[5]

The fission-product pilot plant at Oak Ridge National Laboratory (ORNL) has been cleared for reactivation on a high-priority basis, after a several-month shutdown in connection with last fall's explosion which led to plutonium contamination. The plant plans to recover Sr^{90}, Ce^{144}, Cs^{137}, and Pm^{147} from fission-product wastes. Since the fission-product requirements exceed the supply available at ORNL, other sources are being tapped for feed material. ORNL and Hanford are designing a cask to handle up to 500,000 curies of material taken directly from the Hanford production plants. The material is evaporated for shipment to ORNL.[9]

Completion of a Martin Company processing facility for development of Cm^{242} as a fuel for isotopic power sources was expected by the end of June. Martin plans to develop techniques for encapsulating Am^{241}, which may then be irradiated for about three months in the Materials Testing Reactor (MTR), in Idaho, for conversion to Cm^{242}. Curium is attractive for isotopic power because of high power density, potentially low cost as compared with Po^{210}, and capability for fabrication in fuel forms which meet the requirements of thermionic direct-conversion devices.[8]

Economics

The domestic plutonium repurchase price guaranteed by the AEC through June 30, 1962, is $30 to $45 per gram depending on isotopic purity; for the following year (until June 30, 1963), the guaranteed price is a flat $30 per gram. AEC Commissioner John Floberg recently told Congress: "We have within our legal authority to extend that date [June 30, 1963], but we have never done so and there is no contemplation at the moment of doing it." The price assumed beyond that date, based solely on the reactor value of plutonium, is $12 per gram.[5]

The Canadian Government has issued the following figures for the year 1959 on uranium sales abroad:[5]

Purchasing country	Sales
United States	$278,912,726
Great Britain	32,602,987
West Germany	129,262
Switzerland	121,760
Japan	106,831
India	20,000
Sweden	8,711
Austria	1,591
Denmark	284
Total	$311,904,152

Waste-Disposal Licensing

The AEC has established two interim land burial sites for the disposal of solid, packaged radioactive wastes generated by AEC licensees. The two sites, at ORNL and the National Reactor Testing Station (NRTS) near Idaho Falls, Idaho, have been established pending later designation of permanent land burial sites to serve various areas of the country. Wastes packaged in accordance with Interstate Commerce Commission (ICC) regulations for transport are acceptable for burial. Charges for burial will be at a rate of 70 cents per cubic foot with a minimum charge of $21 for 30 cu ft or less. High-level liquid wastes from fuel processing will continue to be stored in underground tanks at AEC's Idaho Falls, Hanford, Savannah River, and Oak Ridge sites.[10]

Following AEC's designation of the two interim land burial sites, a protest was filed by the Isotopes Specialties Div., Nuclear Corp. of America, against the fact that AEC was not providing for shipment of wastes to the sites via the waste-disposal firms presently handling ocean disposal. Isotopes Specialties claimed that such firms had played a major role in the proper packaging of wastes for shipment to

disposal sites and that the new ruling removes many of the precautions set up for these disposal firms. It was claimed that AEC licensees would now be free to ship wastes to inland sites without the supervision previously provided by the waste-disposal firms.[6]

AEC has issued a decision, dated June 22, 1960, in the matter of Industrial Waste Disposal Corp. of Houston, Texas, an applicant for a license to receive, store, and dispose of packaged low-level wastes, generally resulting from use of radioisotopes in hospitals, research facilities, and industry. The application sought authorization to collect wastes, add further packaging and concrete so that the containers would sink readily, and finally to dispose of the packages in the Gulf of Mexico where the depth is at least 1000 fathoms. The decision authorized the issuance of a license to receive and store specified quantities of waste at the applicant's Houston facility. The AEC did not grant that portion of the application permitting disposal in the Gulf of Mexico, but remanded the case to the Hearing Examiner for further proceedings concerning the integrity of containers and possible relocation of the sea disposal site.[11]

In an order issued May 5, 1960, the AEC suspended the license of the Coastwise Marine Disposal Company to receive by-product, source, or special nuclear material for ocean disposal because of alleged violations of regulations. In a hearing held on May 9, the licensee was allowed until Oct. 1, 1960, to file briefs in response.[5]

Nuclear Engineering Company of Pleasanton, Calif., informed the AEC that the company has been considering the feasibility of disposing of low-level liquid radioactive wastes directly to the Pacific Ocean without packaging. AEC replied that its approval would first be required.[5]

A number of studies and surveys of the safety of radioactive waste disposal in both land and ocean burial areas have been made by AEC and by the International Atomic Energy Agency (IAEA). These are discussed in Section V of this Review.

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11. AEC Issues Decision in Houston Waste Disposal Case, AEC Press Release C-121, June 23, 1960.

Radiation Hazards in Uranium Mills and Mines

Since August 1959 the AEC has been visiting each operating uranium mill to make independent check measurements to permit estimates of the concentrations of radioactive material in dust and liquid waste. Thousands of air and water samples have been taken. According to Curtis A. Nelson, Director of AEC's Division of Inspection, speaking at the Western Mining and Energy Conference in Denver, only "a few mills are apparently close to meeting AEC standards. ...Preliminary data do not show an immediate hazard to mill employees or the public, but show there is still much to be done in a number of mills to reduce dust concentrations." The Joint Congressional Committee on Atomic Energy revealed in April that it had requested AEC to provide a report on uranium mills which would include radiation safety data.[1]

The health hazards posed by the presence of radon and its daughters in the air of uranium mines have been studied by the Bureau of Mines. According to James Westfield, Assistant Director of Health and Safety in the Bureau, no radioactivity problem exists in open-cut mines, but in underground mines mechanical ventilation often had to be installed to reduce radon-daughter concentrations to the working level suggested by the Public Health Service (PHS). Inspection of underground mines since December 1958 revealed three mines at or below PHS suggested concentration levels, six mines at 1 to 3 times suggested levels, four mines at 3 to 10 times suggested levels, and six mines more than 10 times suggested levels. The Bureau of Mines is responsible for inspection of mines on Indian lands only. With respect to other mines, the AEC, Public Health Service, and Bureau of Mines

have adopted the position that the basic responsibility for the enforcement of radiation standards rests with the states. A Committee of the American Standards Association (ASA) has drafted a proposed radiation protection standard for uranium mines and mills which is shortly to be submitted to ASA for approval.[1]

Hearings were held May 16−19 in connection with alleged violations of safety regulations at the Edgemont, S. D., uranium processing mill of Mines Development, Inc. The AEC staff was given until June 20 to file briefs and conclusions.[1]

Shipment of Fissionable Material

A recent article by Lewis and Goin[2] describes safe methods for packaging fissionable materials to prevent possible assembly into a critical mass. Most shipping and storage methods rely on spatial separation only, but these authors recommend that isolation be achieved by separating fuel-bearing materials by a poison-moderator-poison sandwich. The suggested fuel-shipping sandwich is of cadmium foil in the layer closest to the fuel and solid hydrogeneous material (wood or polyethylene) in the outer layer. In effect, fast neutrons originating in a fuel region pass through one layer of poison and are moderated before reaching the second layer, where they are effectively removed. Water also can be considered as a sandwich filler. The authors believe that small samples so packaged could be transported by any means, without special shipping instructions. The same principles apply to compact storage of fuel in a canal or vault and also might be adaptable to fuel-processing plants. Calculations have been prepared for safe slab thickness and cylinder diameter for various thicknesses and types of moderators.[3]

Enriched-Uranium Processing

At the annual indemnity hearings held by the Joint Congressional Committee on Atomic Energy in April 1960, a question was raised as to whether fuel fabricators should be covered under the Price-Anderson Indemnity Act. Although the question referred specifically to fuel fabricators, it might apply equally to future private fuel processors. Harold Price, Director of AEC's Division of Licensing and Regulations, stated that the AEC was attempting to establish whether there is a need to extend government indemnity. Along these lines a report from Convair, which was under contract to make a study for AEC of the potential hazards in the processing of unirradiated, enriched uranium, is being analyzed by the AEC and may serve as a basis for a decision on possible extension of government indemnity.

The Convair report[4] states that, in the 14 years since the inception of processing and fabrication operations with fissionable material, only two nuclear excursions have been experienced. In October 1959, a third accident occurred at the Idaho Chemical Processing Plant (ICPP), a facility which recovers uranium from irradiated reactor fuels. With respect to the magnitude of possible accidents, it is stated that the majority of excursions ("average accidents") will probably lie within a relatively narrow range from 4×10^{16} to 4×10^{17} fissions, if the excursion terminates after the initial power burst. For "maximum" aqueous accidents, yields up to 8×10^{19} fissions are considered possible. (The accident at the Idaho plant was estimated to have produced 4×10^{19} fissions in an excursion of several minutes' duration.) Enriched-uranium metal buttons were calculated to be capable of up to 10^{21} fissions in a single burst. The extreme accident, which might produce an explosion equivalent to a ton or so of high explosives, appears to be far more unlikely than the "average accident."

Concerning the extent of human injury, the report states that the hazard range for one acceptable emergency dose (AED = 25 rem) of single-burst average accidents is less than 100 meters, whereas the lethal range is probably less than 10 meters. In the event of a "maximum accident" of 10^{20} fissions in a single burst, it is likely that most of the persons within a radius of 100 meters would be killed by the blast, flying debris, or radiation. Lethal doses from exposure to the radioactive cloud may be received downwind as far as 300 meters. Some exposures of one AED from the cloud could be received at distances up to 1800 meters.

The results of this study apply only to accidents involving unirradiated, enriched uranium and should not be taken as a measure of the hazard associated with the processing of irradiated uranium.

Irradiated, Enriched Fuel Processing

Facilities originally installed at the Savannah River Laboratory for chemical processing of irradiated fuel were designed to separate and purify irradiated natural uranium and plutonium, segregating fission products for storage as waste. Later, the AEC requested that Savannah River be prepared to separate enriched fuels, such as from the power-reactor program. In order to use large equipment (designed for handling tonnage quantities of natural uranium) for recovery of enriched uranium, it is necessary to employ dilute uranium solutions, keeping the concentration safely below the nuclear critical level at all times. In other words, the avoidance of criticality at Savannah River will not be done by control of equipment dimensions (geometry). A report[5] recently issued discusses the steps that have been taken to reduce the chances of incurring a nuclear incident while processing enriched uranium at Savannah River. Such steps include modification of equipment, provision of special instrumentation to detect accumulations of fissionable material before they could build up to a critical mass, and the fixing of operating procedures.

Over 90 per cent of the equipment to be used in the new process had been operated successfully for more than three years on a similar process and with similar procedural control. The proven reliability and integrity of administrative control of material and procedures were given much weight in the final conclusion that the proposed conditions of operation were safe.

Because of the design of the process building, which included heavy shielding for nearly all the process equipment, and the size of the plant site, a "maximum credible incident," the magnitude of which was calculated from generally accepted principles, would create hazardous conditions only within localized areas confined

within the plant site. It was believed that, under these conditions, the hazards from criticality incidents were not significantly different from the hazards normally involved in the operation of a large, complex, chemical plant processing radioactive material.

Redox Multipurpose Dissolver Incident at Hanford

On April 17, beginning at about 8:45 p.m. and ending about 30 min later, a series of three sharp pressurizations occurred in the new Redox multipurpose dissolver at Hanford, accompanied by rumbling noises and building vibration.[6] At the time of the incident the dissolver contained a sizable quantity of bare uranium, only half of which was covered with water. It is believed that the series of explosions was preceded by the burning of uranium in the dissolver. This is conjectured to have started about noon on April 17, as indicated by an abnormal temperature rise of the water in the dissolver and (as discovered on the following day) by a 300-fold increase in the gamma radioactivity entering the sand filter with the cell ventilation air.

At 6:00 p.m. on April 18 it was noted that the dissolver off-gas temperature was again slowly increasing, as was the radioactivity level of the air entering the sand filter. The dissolver contents were therefore quenched with a large volume of water to prevent a possible repetition of the reaction. Procedures are currently in preparation for the slow, cautious dissolving of the contents of the vessel.

There was no spread of radioactivity either to the occupied zones of the building or to the plant environs. There were no injuries and no radiation exposures to personnel. The full extent of damage is not yet known but appears to be confined to the internal steam coil and a hole in the shell of the vessel proper. It is possible that some of the auxiliary equipment may also be damaged.

The causes and mechanisms have not yet been established, but intensive study is being carried out, and a detailed technical analysis will be presented in a future report. It is currently assumed that the bare fuel elements exposed to the humid atmosphere reacted spontaneously with air and/or water vapor at a rate in excess of the capability of the system to remove heat. The geometry of the new dissolver differs considerably from conventional Hanford dissolvers.

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PREPARATION FOR FUEL PROCESSING

The large number of fuel alloys and cladding materials and the multiplicity of fuel-element designs make it difficult to accommodate power-reactor fuels into solvent-extraction processing plants as they exist. Accordingly, a number of "head-end" processes are being considered in order to prepare, from the wide variety of fuels, fuel solutions which are compatible with existing plants. Some processes remove the cladding separately; some put cladding and fuel into a single solution. Information on mechanical decladding, chemical dejacketing, and dissolution procedures is presented in this section.

A recent listing of reports in the field of fuel processing has been compiled by Jacobs.[1]

Mechanical Processing

Mechanical methods of removal or destruction of fuel-element cladding often permit conventional nitric acid dissolution of the declad fuel. Shearing and sawing methods of fuel-element disassembly being examined at Hanford Atomic Products Operation (HAPO) have been discussed in previous reviews.[2-4]

At Hanford the primary objectives of the mechanical treatment facility are (1) the removal of end fittings and minor disassembly as required to permit charging of the fuel element to a dissolver and (2) the inspection of solid residues from the dissolver. Somewhat less emphasis will be placed on development of a shear for size reduction to permit a larger charge to the dissolver and, hence, greater processing capability, and to permit core leaching should fuel elements be received which resist applicable chemical decladding processes.

Recent Hanford reports[5-8] indicate that interim or summary reports on essentially completed phases of the work are being issued as follows: HW-62842, Shear Studies for the Non-

production Fuels Processing Program; HW-62843, Interim Report: Hacksaw Studies for Power Reactor Fuels Reprocessing; and HW-65380, Yankee Bandsaw Cutting. A report already issued[9] discusses high-speed saw tests for hardware cutoff. Both the economic feasibility and adaptability of the friction saw, at least for hardware, were demonstrated by the studies. However, two disadvantages were also noted which must be considered in equipment selection for the power fuels-processing facility:

1. Since the friction blade cuts by melting metal, high temperatures exist in the vicinity of the blade. With high temperatures, ignition of potentially pyrophoric fissile core materials is possible.

2. Friction blade sawdust (and, indeed, any high-speed blade sawdust) is very fine. Filtration studies showed that 25 per cent of the friction sawdust is smaller than 35μ; 3 per cent is submicron. High-efficiency filtration equipment would be required for dust control with the high-speed saw.

At ORNL the initial operability tests of equipment for dejacketing the Sodium Reactor Experiment (SRE) NaK-bonded stainless-steel-clad uranium fuel rods were successful.[10-12] In fuel leaching tests[11,13] the effective area of cylindrical uranium dioxide pellets dissolving in nitric acid was estimated from experimental rate measurements as a function of the fraction dissolved. The results can be approximated by

$$A_p/A_0 = 1 + 13X - 14X^2$$

where A_0 is the area of initial cylinder ($D/L \approx 1$); A_p is the effective area of porous, partially dissolved pellet; and X is the fraction dissolved, by weight.

Remotely operated, semiautomatic machines, designed to effect the mechanical disassembly

(i.e., decanning) of spent fuel elements from the Experimental Breeder Reactor (EBR-II), are under development at Argonne National Laboratory (ANL).[14] The machines described are laboratory models which are being tested on simulated fuel elements. They are electrically or pneumatically operated and are capable of decanning three fuel elements per minute. In the first of the two machines described, pneumatically operated devices prepare the fuel element for a rotary shearing operation which cuts the tubing jacket along a helical circumferential path as it is being removed. The alternate machine removes the jacket by means of a series of shearing rolls. Both machines are served by auxiliary mechanisms, such as inspection jigs, fuel and scrap choppers, and transfer magazines. These units are located to eliminate handling between steps of the decanning operation and are designed for easy removal for replacement or maintenance. Improved versions of these machines or other machines employing alternate methods still under development are to be designed for installation in the fuel-cycle facility of the EBR-II plant.

The proceedings of the AEC symposium on chemical processing of irradiated fuels for power, test, and research reactors, held in Richland, Wash., on Oct. 20 and 21, 1959, have been published as USAEC Report TID-7583. In this document, papers are included in which the mechanical operations contemplated at Hanford,[15] Idaho,[16] Savannah River,[17] and Oak Ridge[18] for the interim processing of various power-reactor fuels are described.

Chemical Dejacketing

Chemical dissolution of fuel jackets and structures is an attractive alternate to mechanical dejacketing or complete chemical dissolution of fuel. The exposed fuel cores can then be dissolved by another reagent in a second step. The principal materials used for cladding are aluminum, zirconium or Zircaloy, and stainless steel.

Decladding methods for various reactor fuels were discussed at the Richland symposium by Platt,[19] Hull,[20,21] Blanco et al.,[22] and Irvine.[23]

Removal of Zirconium and Zircaloy Jackets

The Zirflex process may be used to dejacket zirconium-clad or Zircaloy-clad fuel elements

having oxide cores. The Zirflex process is applicable to the processing of fuels from the Dresden boiling-water reactor and the Shippingport pressurized-water reactor (PWR).[24,25] Other applications are to fuels from the Plutonium Recycle Test Reactor (PRTR) and the New Production Reactor (NPR), both at HAPO; to possible fuels from the EBR at Arco, Idaho; and to fuels from the Canadian NPD-2 reactor and the Carolinas-Virginia Nuclear Power Associates reactor.

Recent studies at Hanford[5-7] have been concerned with defining the dependence of Zircaloy-2 dissolution rate on hydrogen-ion concentration (pH) during decladding by the Zirflex process. Data obtained so far indicate the dissolution rate to be proportional to $(H^+)^{0.68}$. Preliminary data on the dependence of Zircaloy dissolution rate on free-fluoride concentration indicate the rate to be proportional to $(F^-)^{1.6}$ at pH 7.

Study was continued at Hanford on a Zirflex process modification in which reaction-generated ammonia is neutralized by addition of hydrofluoric acid instead of being removed by volatilization.[5] Zircaloy-clad uranium dioxide fuel elements simulating those expected in the PRTR, and which had been autoclaved to produce a "black oxide" coating, were declad in a solution initially $2M$ ammonium fluoride—$0.5M$ ammonium nitrate. At pH 7.6, rapid attack on the Zircaloy-2 did not occur until after an induction period ranging from 50 to 90 min. Dissolution then proceeded by pitting attack and undercutting characteristic of Zirflex dissolution of oxide-coated Zircaloy-2.

Runs were made to demonstrate the Zirflex decladding of oxidized PRTR fuel elements (Zircaloy-2-clad UO_2) in a recirculating dissolver.[7] Dissolvent charge concentrations were $5.5M$ ammonium fluoride plus $0.5M$ ammonium nitrate with a fluoride-to-zirconium mole charge ratio of 7. A steam sparge was used in the first run, and an air sparge was used in the second so that uranium core losses to the decladding wastes could be compared for the two methods. The fuel-element cladding, including end plugs and hangers, was completely dissolved in less than 6 hr in both cases. For the steam-sparged run, uranium losses were approximately 0.7 g/liter or 0.33 per cent of the charge. Losses for the air-sparged run were increased by approximately a factor of 3 to 2.0 g/liter or 0.85

per cent of the uranium charge. These losses were higher by a factor of 10 and 28 than the losses from the steam-sparged dissolution of unoxidized elements reported earlier,[6] possibly because of the typical uneven penetration always secured with oxidized elements. Laboratory-scale decladding experiments with oxide-coated elements verified the results obtained in pilot-plant runs with the dissolver using recirculation.

Using the same dissolvent, sections from extruded NPR fuel end rejects were declad in a batch tubular dissolver. An average boilup rate of 0.25 lb-mole/(hr)(sq ft) based on initial Zircaloy surface area was maintained. A dissolution time of 3 hr was not sufficient to dissolve all of the massive Zircaloy but was long enough to expose approximately 90 per cent of the uranium-metal core. Losses to the Zirflex decladding waste were less than 0.5 per cent for this type of operation. It will be necessary to charge about 10 per cent excess of fluoride and to operate approximately 4 hr in order to declad the uranium completely. Final dilution of up to 200 per cent of the charge solution is necessary to avoid zirconium precipitation.

An alternate process for dissolving Zircaloy-2 cladding in hydrofluoric acid—nitric acid solutions is being studied.[5,6] This process seeks to take advantage of low corrosion rates observed for nickel-base alloys and relatively high Zircaloy-2 dissolution rates in nitric acid—hydrofluoric acid solutions at low temperature (25 to 50°C). Preliminary data indicate satisfactory Zircaloy-2 (unoxidized) dissolution rates (10 to 15 mils/hr) can be achieved with $2M$ hydrofluoric acid—$0.25M$ nitric acid: corrosion rates of less than 1 mil/month for Battelle Memorial Institute (BMI) experimental alloy 11B were obtained under similar conditions. Higher hydrofluoric acid concentrations ($3M$) were required to penetrate oxidized Zircaloy in reasonable times. Oxide films on Zircaloy which had been exposed to high-temperature water were penetrated more slowly by acid fluoride decladding solution ($0.25M$ nitric acid—$3M$ hydrofluoric acid, 25°C) than by boiling Zirflex decladding solution.

Attack of uranium dioxide core materials by typical terminal decladding solutions ($0.25M$ nitric acid—$2M$ hydrofluoric acid—$0.44M$ zirconium) was relatively high, about 0.1 wt.% per hour for the sample studied. The attack was reduced markedly by addition of nitrite inhibitors such as sulfamic acid and urea to the decladding solution. However, when these agents are present during the decladding step, uranium losses are increased.

Studies of the Zirflex process and the barium fluozirconate process are also being made at ICPP.[26-28] The latter process involves separation of zirconium from dissolver solution by adding barium ion, either as a solid barium compound or as a concentrated solution to a high-zirconium alloy dissolver solution ($1.7M$ zirconium, $1.9M$ acid, and $8.7M$ fluoride). In experiments in which the barium was added as an equimolar mixture of the fluoride and nitrate (both solid), the zirconium concentration in the supernatant was reduced to $0.1M$ in 4 hr with the precipitation of the fluozirconate, presumably the $BaZrF_6$.

Removal of Stainless-Steel Jackets

A literature survey made at ORNL of the thermodynamics and limits of flammability of gases expected to be generated during the Darex (dilute aqua regia) and Sulfex decladding of stainless-steel-clad NaK-bonded fuels indicated that vapor-phase explosions are a definite possibility with the Darex ($5M$ nitric acid—$2M$ hydrochloric acid) system when used with NaK-bonded fuels.[10] Reactions between nitrogen oxides and hydrogen are highly exothermic, and mixtures of the gases are explosive over wide concentration ranges.

The hydrogen content of Darex off-gases from dissolution of stainless-steel-clad oxides is very low. Measurements show that the hydrogen content of the off-gas from batch dissolution of type 304 stainless steel increased with increasing hydrochloric acid concentration. The average increase was from 0.14 per cent with $5M$ nitric acid—$2M$ hydrochloric acid to 2.5 per cent with $1M$ nitric acid—$6M$ hydrochloric acid; the maximum concentration from the latter dissolvent was 4 per cent for 30 per cent metal dissolution.

Four decladding tests were run in engineering-scale equipment on unirradiated prototype Consolidated Edison fuel (thorium dioxide—uranium dioxide with stainless-steel cladding) assemblies to determine reaction rates, dissolution rates, decladding time, product loading, cross contamination of the cladding and core dissolvents and its effect on passivation, and thorium

and uranium losses to the decladding solution.[10,11] The results of the runs showed average decladding rates of 1.64 and 2.27 mg/(cm^2)(min) with 660 and 530 per cent excess boiling 4M sulfuric acid; instantaneous rates varied from 2 to 51 g/min. The cladding-solution metal loading varied inversely with dissolvent flow rate and ranged from 35 to 27 g of stainless steel per liter. From 2.78 to 4 hr was required for decladding. The average nitrate concentration in the cladding solution from cross contamination was approximately 0.004M; the sulfate concentration in the core solution varied from 0.001M to 0.006M. Instantaneous nitrate concentrations in the cladding solution varied from an initial value of 0.015M to a final value of 0.0005M. Thorium and uranium losses to the decladding solution varied from 0.017 to 0.08 per cent in the absence of a heel to 0.08 to 0.2 per cent in the presence of a heel. These losses were somewhat lower than those reported in the previous Review[4] for work done at BMI.

The Sulfex process is also being investigated at Hanford.[5-7] Qualitative experiments have demonstrated that nitrate in 4M sulfuric acid can be destroyed with Formalin to the extent that active stainless steel is not passivated by the solution.[5] A study of the effects of irradiation of uranium dioxide on stainless-steel heel and on dissolution rate in sulfuric acid was made in order to find reasons for core loss to the decladding solution.[29] The rates at which samples of irradiated uranium dioxide and uranium metal dissolved in sulfuric acid were determined under various conditions. Parallel experiments were performed with unirradiated materials to determine the magnitude of any effects of irradiation history as well as to gain a more complete knowledge of the factors influencing the rates of reaction.

The major conclusions of this work are:

1. Irradiated uranium dioxide dissolves more rapidly than does unirradiated uranium dioxide in sulfuric acid. The rate of dissolution of irradiated uranium dioxide is still quite low, however, being only 0.02 per cent per hour in boiling 4M sulfuric acid with uranium dioxide having a level of radioactivity within a factor of 2 or 3 of uranium dioxide fuels expected to be encountered in the nonproduction fuel (NPF) program.

2. The rate at which uranium dioxide dissolves in sulfuric acid is decreased by the presence of dissolving stainless steel.

3. The rates at which uranium dioxide and uranium metal dissolve in sulfuric acid are greater when Fe(III) is present in solution.

4. Exposure of uranium dioxide to air results in the formation of a species, presumably U(VI), which dissolves rapidly in sulfuric acid.

5. Irradiated uranium metal was found to react at the same rate as unirradiated metal in boiling 4M sulfuric acid.

In the electrolytic dissolution of stainless steel in nitric acid at the ICPP,[26] analysis of the effects of current density, cell temperature, and hydrogen ion in the dissolver product has shown the cell voltage to be about 20 per cent higher at 40°C than at 90°C at an interelectrode solution velocity of 1.8 g/(cm^2)(sec). There was some evidence of concentration polarization at 1.2 amp/cm^2 on the fuel and 0.4 amp/cm^2 on the cathode. Cell potential was increased by 7 per cent as the solution hydrogen ion decreased from 5M to 1M and the nitrate ion from 8.6M to 4.6M. The over-all dissolution stoichiometry expressed as equivalents of hydrogen ion disappearing per equivalent of metal dissolved was insensitive to temperature between 40 and 90°C; insensitive to current density, 0.4 and 0.1 amp/cm^2 on the cathode; but varied significantly with solution hydrogen-ion concentration. Values of 1.33 and 1.45 equivalents/equivalent were obtained at 1M and 5M acid, respectively.

Removal of Aluminum Jackets

Procedures for dissolving the nickel coating, proposed for aluminum-clad production fuel elements to increase the corrosion resistance, were discussed in an earlier Review.[2] Further studies on the dissolution of full-size nickel-coated aluminum-clad fuel elements were made. These elements had nickel coating on both sides of the aluminum cladding. They had been heated at 590°C for 45 sec in one step during fabrication. The inner and outer nickel coatings were not attacked by boiling sodium hydroxide–sodium nitrate decladding solution. Underlying aluminum was attacked through imperfections in the nickel coating. Boiling 1M nitric acid attacked the outer nickel coating slowly (3 hr was required to remove the coating). Boiling 1.5M uranyl nitrate –1.5M nitric acid removed the coating before the solution reached boiling. Aluminum cladding was removed readily by boiling sodium hydroxide–sodium nitrate.

Dissolution

Simultaneous Dissolution of Jacket and Core

Zirconium Fuel Elements. It has been proposed that uranium—low zirconium alloys be used as fuel in the NPR reactor. A survey to determine the problems associated with processing such fuels in the Redox plant is in progress at Hanford.[T] Studies to date have been made with uranium—2 wt.% zirconium alloy. Of concern is the possible formation of explosion-sensitive surfaces on uranium-zirconium alloy when dissolved with nitric acid only. Such surfaces are formed on alloys containing from 5 to 25 per cent zirconium. The lower limit of zirconium content for sensitive-surface formation is not well defined. Attempts to form such surfaces on uranium—2 wt.% zirconium alloy have been successful only when the alloy was given a prolonged (three weeks) heat-treatment at 575 °C before dissolving it in nitric acid. Reproducibility was poor even with this treatment.

Dissolution rates for the uranium—2 wt.% zirconium alloy in nitric acid only were very low compared to rates for uranium metal under similar circumstances. Penetration rates decreased from about 1 mil/hr in boiling $10M$ nitric acid to 0.1 mil/hr in $2M$ nitric acid—$1.75M$ uranyl nitrate.

The only procedure currently available for preventing sensitive surfaces on uranium-zirconium alloys during dissolution in nitric acid is to add fluoride ion. Several studies have shown that the concentration of fluoride must be at least four times that of the dissolved zirconium. However, to use this procedure in the Redox 300-series stainless-steel dissolvers, it would be necessary to protect the dissolvers against severe corrosion by the nitric acid—hydrofluoric acid mixture. Aluminum ion in an aluminum-to-fluoride mole ratio of 1 or more is effective. Previous studies have shown that, when aluminum ion is present, the mole ratio of fluoride to dissolved zirconium must be greater than 4. Based on these requirements, a test flow sheet having terminal dissolver solution composition $1M$ uranyl nitrate—$1M$ aluminum nitrate—$0.8M$ fluoride—$0.05M$ zirconium was proposed. Although synthetic solutions with this composition and with free nitric acid from $0M$ to $0.8M$ were stable toward solids formation, solid-free solutions could not be obtained in attempts to dissolve uranium—2 wt.% zirconium

alloy to terminal solutions of this composition. Dissolution rates for uranium—2 wt.% zirconium in these solutions, although higher than in nitric acid only, were still low compared to the dissolution of uranium metal in nitric acid.

Stainless-Steel Fuel Elements. One of several chemical dissolution schemes proposed for stainless-steel-clad uranium or uranium dioxide is the Niflex process, which uses a nitric and hydrofluoric acid solution for total dissolution.

The nitric and hydrofluoric acid system has been used industrially as a metal pickling agent, but it has not been applied generally to the total dissolution of stainless steel. Consequently the application of the Niflex process for the dissolution of stainless-steel-clad fuels was studied on a pilot-plant scale.[30] The Niflex process employs $1M$ to $2M$ nitric acid and $2M$ hydrofluoric acid for the dissolution of 304L stainless-steel cladding. Dissolution rates for stainless steel are initially 10 mils/hr but decrease markedly after the first hour. As a result, 2 to 5 hr is required to dissolve a 10-mil cladding.

To obtain complete dissolution, a fluoride-to-stainless steel mole ratio near 6 is needed. At the end of the decladding reaction, a stainless-steel concentration near $0.4M$ is normally attained.

Following the dissolution of the cladding, aluminum nitrate is added to complex the fluoride and thereby inhibit corrosion of the dissolver during the dissolution of the core in nitric acid. Core dissolution rates for sintered uranium dioxide average 50 to 70 mils/hr, and metallic uranium rates average 30 mils/hr. At the end of the core dissolution, the stainlesss-steel concentration is about $0.2M$ and the uranium concentration ranges up to $0.5M$.

Equipment corrosion is a major problem with the Niflex process (see the discussion of corrosion in Sec. IV).

Alloy Fuel Elements of Aluminum-Plutonium-Silicon-Nickel. It was reported previously[4] that the Al-Pu-Si-Ni alloy fuel currently being prepared for the PRTR dissolves rapidly in mercuric nitrate—nitric acid solutions of low ($1M$ to $3.5M$) acid concentration but slowly at higher acid concentration. A series of dissolutions of Al-Pu-Si-Ni-Fe alloy was made at Hanford to determine if the rapid dissolution of this alloy in mercuric nitrate—nitric acid solutions at low acid concentrations (about $3M$) could be moderated by the presence of uranyl nitrate.[T] Modera-

tion of the dissolution rate is desired because of hydrogen production. These runs demonstrated that good control of dissolution rate is feasible. Dissolution times for $\frac{1}{2}$-in.-diameter rods were increased from 1 to 24 hr as uranyl nitrate concentration was increased from $0M$ to $0.75M$.

Dissolver solutions prepared by dissolving aluminum − 2 wt.% plutonium − 2 wt.% nickel alloy in nitric acid − mercuric nitrate − uranyl nitrate solutions were visibly clear and free of solids. Dissolution rates were comparable to those for the Al-Pu-Ni-Si-Fe alloy used in previous studies.

Dissolution of Dejacketed Material

If fuel jackets are previously removed by mechanical or chemical means, the core may be dissolved by a simple chemical procedure. The addition of boric acid as a soluble nuclear poison during dissolution of uranium-molybdenum fuels in nitric acid − ferric nitrate solutions has been suggested at Hanford.[6] Addition of Formalin to destroy the excess acid resulting when uranium-molybdenum alloys are dissolved in strong nitric acid was successfully tested.[5] The addition of strong nitric acid was necessary to dissolve the precipitates formed in nitric acid − ferric nitrate dissolutions.

In studies at ORNL the dissolution of uranium − 3 per cent molybdenum alloy in boiling $3M$ to $11M$ nitric acid resulted in the consumption of 4 to 7 moles of acid per mole of alloy dissolved; with $5M$ nitric acid containing up to $1M$ ferric nitrate, 4 moles of acid was consumed per mole of alloy dissolved.[12] Pure molybdenum dissolved at a rate of 1.8 mg/$(cm^2)(min)$ in refluxing $18.3M$ sulfuric acid. The rate decreased to nearly zero as the acid concentration was decreased to $14M$ or increased to $20M$.

In dissolution tests with uranium − 8.4 per cent molybdenum alloy fuels, 3 to 4 moles of nitric acid was consumed for each mole of alloy dissolved in nitric acid or nitric acid − ferric nitrate.[11] The solutions produced contained $0.25M$ to $1M$ iron and $0.3M$ to $2M$ uranium. These results are valid only for the experimental conditions used, since the amount of acid apparently consumed is partially governed by the efficiency of the off-gas condensing system.

The recovery of uranium and thorium from graphite fuels is being examined at ORNL. A method of simultaneously disintegrating to 20-mesh material and leaching the uranium from small pieces of graphitized fuels by boiling in fuming nitric acid (90 per cent nitric acid, 0.2 per cent maximum dissolved oxides) was developed.[10] Two successive acid treatments followed by water washing recovered not less than 99.85 per cent of the uranium in fuels containing 5 per cent or more uranium; recovery decreased to 99 per cent when the uranium concentration in the fuel was only 2 per cent. When 70 per cent acid was used instead of 90 per cent in the second leach, metal recoveries decreased by at least 0.2 per cent.

Samples of graphite − uranium carbide fuel were disintegrated and leached twice at 25°C with 90 per cent fuming nitric acid.[11] Recovery of uranium from fuel containing 2 per cent or more uranium was 99.5 per cent as compared with 99.8 per cent recovery for a 90 per cent nitric acid disintegration and leach followed by a secondary leach with boiling $15.8M$ nitric acid. The uranium recovery from all fuels studied was independent of the temperature of the first leach with 90 per cent acid between 25°C and the boiling point ($\sim$103°C). Since 25 to 30 per cent of the total uranium recovered was found in the wash solutions, high recoveries can be achieved only after thorough washing of the graphite matrix. These tests indicate that adequate uranium recovery may be achieved at 25°C with 90 per cent nitric acid and water washing alone, thereby minimizing both corrosion of stainless steel and formation of colored, nitric acid − soluble, graphite degradation products.

Five successive 4-hr leaches of 15-g specimens of graphitized uranium-graphite fuel with 70 per cent nitric acid resulted in the recovery of 60 per cent of the uranium in fuel containing 0.7 per cent uranium, 64 per cent for 2.5 per cent uranium fuel, and 75 per cent for 5 per cent uranium fuel.[12] No swelling or disintegration of the graphite occurred. The same fuels were disintegrated and leached with two portions of boiling 90 per cent nitric acid; uranium recoveries were 97, 99.5, and 99.85 per cent, respectively.

Iodine monochloride disintegrated samples of 10 and 14 per cent uranium-graphite fuels to 20 mesh; but the halogen, primarily iodine, could not be readily removed from the graphite and inhibited the subsequent nitric acid leaching.[12] Two leaches with $15.8M$ nitric acid recovered

97 per cent of the uranium from the 14 per cent fuel and only 85 per cent from the 10 per cent fuel. Disintegration and leaching with 90 per cent nitric acid recovered 99.95 per cent of the uranium from similar specimens of these fuels.

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RESEARCH AND DEVELOPMENT
ON FUEL PROCESSING

Solvent Extraction

The proceedings of the AEC symposium on fuel processing, held in October 1959 at Richland, Wash., have been published[1] as USAEC Report TID-7583. That document gives the plans for the interim processing of irradiated fuels from power, test, and research reactors, and it merits serious study.

Modification of Purex and Redox Processes

The Purex (TBP extractant) and Redox (methyl isobutyl ketone extractant) processes have proved to be the most tractable and economical methods available for the large-scale recovery of uranium and plutonium from irradiated natural uranium. However, the adaptation of Purex and Redox technology to high-burnup nonproduction reactor fuels is not a simple task. An important problem is radiation damage to extractants and diluents. Perhaps an even more important problem is the preparation of aqueous feed solutions providing the nitric acid environment required for the Purex process or the neutral or acid-deficient environment needed for the Redox process.

Hanford has been assigned the responsibility for the processing of a number of low-enrichment nonproduction reactor fuels. Among these are uranium-molybdenum alloys containing 3 to 10 wt.% molybdenum. A topical report covering the progress in the development of a process to recover and purify the uranium in these fuels by Redox processing is available.[2] Some comments on this work as reported in various progress reports were presented in a previous Review.[3] The highlights of the topical report are briefly reviewed herein. Feed solutions 0.3M to 0.7M acid deficient were prepared by treating dissolver solution with sodium hy-

droxide or dibasic aluminum nitrate. However, ferric ion, present in the feed solution, slowly hydrolyzed, and thus the end result was a feed more acidic than normal Redox feeds. The source of iron was the ferric nitrate—nitric acid fuel-element dissolvent. In countercurrent solvent-extraction runs with feed solutions spiked with fission-product activity, decontamination factors were lower by a factor of 5 than those realized with normal feeds. Uranium and plutonium recoveries were about the same as those realized with standard feeds.

In the solvent-extraction process, ferrous sulfamate is widely employed to reduce plutonium to Pu(III) in the uranium-plutonium partition cycle. A disadvantage of the use of ferrous sulfamate is that it represents the introduction of a foreign metallic ion in the waste stream. A study has been made of the use of uranous salts to achieve the required plutonium reduction.[4] The stability of uranous ion with and without the use of a sulfamic acid stabilizer was studied in typical extraction systems. With a stabilizer present, the use of uranous ion was successfully demonstrated in the decontamination of uranium from traces of plutonium. Under typical Purex conditions, however, the uranous ion was not a satisfactory reductant because of excessive contamination of the plutonium product with uranium.

The typical Purex extractant employed in the United States is 30 per cent TBP diluted with kerosene. After an exhaustive development program, however, the French settled on an extractant containing 40 per cent TBP. Studies are being made in this country to determine the advantages to be gained, if any, by the substitution of 40 per cent TBP in kerosene for the 30 per cent TBP extractant now employed in the Thorex process. In demonstration runs a flow sheet based on 40 per cent TBP produced

equal decontamination, lower waste volume, and possible increased plant capacity. Satisfactory partition of uranium and thorium was obtained in five strip and five scrub stages.[5]

The application of a Purex modification to the separation of transplutonium elements from rare earths has been demonstrated in a multi-stage contactor. Relative extraction coefficients in the system TBP—$9.9M$ lithium chloride, $0.1M$ hydrochloric acid were: 1, 2, 2, 7, and 35 for cerium, europium, yttrium, americium, and lutetium, respectively.[6]

Work, which could have application to the recovery of fission-product activities, is in progress at the Ames Laboratory. The separation and recovery of barium and strontium chlorides in a system of sodium thiocyanate or ammonium thiocyanate, water, and TBP have been successfully demonstrated.[7] Sodium thiocyanate was the most effective salt. Strontium was recovered in the organic phase, and barium was recovered in the aqueous phase. With other variables constant, the amount of both barium and strontium transferred to the organic phase increased sharply with the thiocyanate up to a concentration equal to the total barium and strontium equivalent concentration.

Studies of Alternate Extractants

Several classes of organonitrogen and organo-phosphorus compounds exhibit unusually high extraction power and selectivity for metal ions and complexes in aqueous media. In addition, many of these compounds show greater resistance to radiation damage than TBP. Work continues on the adaptation of these extractants to various fuel-processing needs.

The application of amine extractants to the recovery of metal ions from nitrate solutions is being systematically pursued at the Massachusetts Institute of Technology, Nuclear Engineering Department, under subcontract to ORNL.[8] Extraction studies have been made for molybdenum, zirconium, samarium, and ruthenium with trilaurylamine (TLA), bis(1-iso-butyl-3, 5-dimethylhexyl) amine (Amine S-24), ditridecylamine (DTDA), and trialkylmethylamine (Primene JM). Molybdenum extraction coefficients with $0.1M$ amine in toluene varied from about 100 in $0.01M$ acid to about 10^{-4} in $2M$ nitric acid. Zirconium and samarium extraction coefficients with $0.3M$ amine were less than 10^{-2} at aqueous-phase nitric acid concen-

trations between $2M$ and $8M$. The ruthenium extraction coefficient with $0.1M$ amine was less than 0.1 for all concentrations from $2M$ to $8M$.

The extraction of technetium and neptunium from uranium hexafluoride transfer-cylinder wash solutions has been demonstrated in countercurrent contactors using a commercial tertiary amine. Neptunium, technetium, and uranium were coextracted with trilaurylamine. Values were stripped consecutively: uranium with $0.5M$ nitric acid, neptunium with $0.1N$ sulfuric acid, and technetium with $1.0M$ ammonium hydroxide. About 1.5 per cent of the technetium accompanied the uranium product. The process was time-dependent in that the neptunium contamination of the uranium product was greater from aged solutions than from fresh extracts.[5,9]

Much of the work being done with organonitrogen compounds has as its primary objective the extraction of values from ore leach liquors. Frequently the results of these investigations suggest methods for attacking some of the more untractable nonproduction reactor fuels. A good example is the use of amines to process aqueous solutions containing uranium and molybdenum. Data were obtained using alamine 336, tri(iso-octyl)amine (TIOA), and a branched secondary amine bis(1-nonyldecyl) amine (XE-204) to compare the efficacy of uranium stripping with ammonium sulfate in the pH range of 3.5 to 4.5. Alamine 336 proved to be the most satisfactory extractant. However, with alamine 336, stripping was relatively difficult below a pH of 4 because of emulsification problems in the mixer-settler contactors. At lower pH, 3.3 to 3.8, physical operations were satisfactory, but excessive amounts of molybdenum were stripped with the uranium products. The aqueous phase employed in the studies contained, in grams per liter, 1.23 uranium, 0.7 vanadium, 0.036 molybdenum, 1.0 iron, 2.3 iron-3, 2.3 aluminum, 0.9 phosphate ion, and 45 sulfate ion. Uranium was stripped from the extract with $1.2M$ to $1.6M$ ammonium sulfate adjusted in pH by the addition of $3M$ ammonium hydroxide.[10]

It has been shown that strontium can be extracted from Purex aqueous waste with di-2-ethylhexyl phosphoric acid (D2EHPA). However, this earlier work employed synthetic waste which did not contain fission-product activities. Recent studies have been directed toward the elucidation of the behavior of fission activities under a variety of conditions.[6]

The extractant is 0.3M D2EHPA–0.15M TBP in kerosene (Amsco 125-82). As shown in Fig. 1, the results of this investigation revealed wide variations in the extraction coefficients of
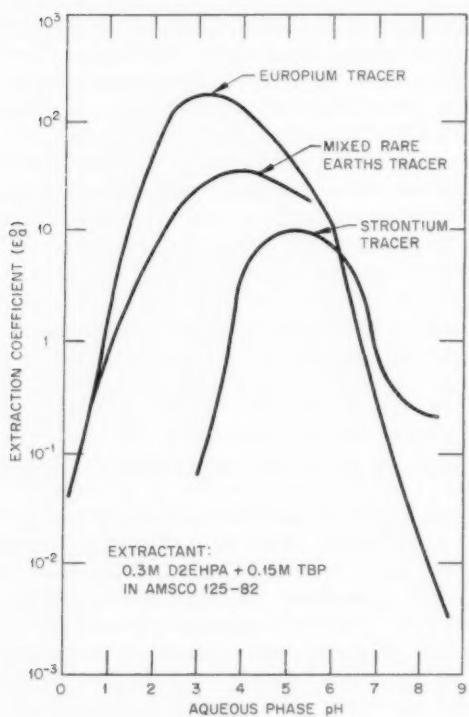
Figure 1—Extraction coefficients for strontium and rare earths with D2EHPA extractant.[6,8]

europium, mixed rare earths, and strontium with aqueous pH. By proper selection of the aqueous-phase pH, it is possible either to extract rare earths and strontium together or to separate them. The authors recommend as the most promising process the simultaneous extraction of strontium and rare-earth activity from aqueous solution at a pH of 5 to 6 followed by selective stripping at adjusted pH in a second cycle.

The process requires the addition of tartrate to the waste solution to prevent the precipitation of iron. In 0.5M to 4M acid and in the absence of tartrate, extraction coefficients for zirconium-niobium were less than 0.5. With 0.5M tartrate present the extraction coefficients were higher and sensitive to the acid concentration. Extraction coefficients observed for

1M and 2M aqueous-phase acid concentrations were 1 and 3, respectively. Coefficients of this magnitude do not preclude adequate scavenging of zirconium-niobium activities. It was noted, however, that the zirconium-niobium extraction coefficients were time-dependent. In extractions from an aqueous solution 2.0M in nitric acid and 0.25M in tartrate, the extraction coefficient increased from 1.0 after 1 min of contacting to 3.3 after 10 min of contacting.[6]

Comparative tests of di-sec-butylphenyl phosphonate (D-s-BPP) and D2EHPA for the uranium-thorium separation showed D-s-BPP to be superior. Thorex-U^{233} product containing about 150 g of uranium per liter was effectively extracted from thorium impurities by solvent extraction with 1.0M D-s-BPP in Solvesso-100 (an aromatic diluent). Complete uranium extraction with less than 2 per cent thorium extraction was observed; this indicates that thorium decontamination factors in the order of 50 are feasible.[8]

Solvent Degradation

Process solvents are degraded by chemical and radiation damage. Satisfactory extractants for high-burnup nonproduction fuels must exhibit acceptable levels of resistance to degradation. Purex and Redox extractants border on being unacceptable. For these processes, however, the required technology has already been developed and demonstrated for several years in production facilities. Therefore they will be used to process the fuel from most of the nonproduction reactors in operation or under construction. Other organophosphorus and organonitrogen compounds are being investigated as alternate extractants. In addition to their greater versatility as extractants, they are, in many cases, more resistant to degradation than either TBP or hexone.

Considerable experimental data have been accumulated on the degradation of the Purex extractant and its diluents. Much of the current work does not appear to provide new knowledge. Some new data are available on the radiolysis of Solvesso-100 which is being considered as an alternate to kerosene (usually Amsco 125-82), the most popular Purex diluent. Comparison of the diluents showed that on irradiation Solvesso-100 produced one-seventh as much gas as Amsco. However, the radiation-induced carbon-carbon unsaturation was twice that of

Amsco 125-82. As shown in Table IV-1, unsaturation leads to greater retention of radioiodine in the diluent. Other results showed[11] that under irradiation TBP-Amsco produced four times as much acid as TBP—Solvesso-100.

Table IV-1 IODINE RETENTION BY PUREX DILUENTS[11]

Material	Iodine absorbed	Double-bond G value $(C=C)$ produced per 100 ev of irradiation
Amsco	7.9	Unirradiated
Solvesso-100	28.4	Unirradiated
Amsco (irradiated)	18.3	2.75
Solvesso-100 (irradiated)	51.4	6.06

Another recently issued report deals with the purification of radiation-damaged Purex solvent. This report also provides a good source of data on the radiolysis products of TBP—Amsco 125-82. The authors conclude that degraded extractant can be purified by a distillation process. Studies with tracer activity showed that the extraction, scrubbing, and stripping characteristics of irradiated solvent, which had been purified by aqueous scrubbing followed by distillation, were similar to those of fresh solvent.[12]

The interest in Solvesso-100 as an alternate diluent in the Purex process emphasizes the need for careful assessment of the effect of double-bond formation on extractant performance. Solvesso-100 is an aromatic compound which under irradiation forms double bonds at twice the rate of kerosene. Studies of the fixation of iodine by irradiated solutions of TBP in various diluents showed that the presence of less than 1 per cent aromatic or olefinic hydrocarbons did not increase the iodine retention. The concentration of TBP in the range studied, 0 to 20 per cent, had no effect. No data were obtained on pure aromatic diluents. The data for kerosene and dodecane are presented[13] in Fig. 2.

In most respects Solvesso-100 is more stable under irradiation than Amsco 125-82. Data presented in Table IV-2 compare the radiation damage to D-s-BPP, and TBP as the extractants and as diluted extractants. Extractants and diluents were irradiated with 1-Mev electrons to 1.08×10^{22} ev per gram, and the yields of total gas, monobasic acid, and dibasic acid were measured. For the pure diluents, the
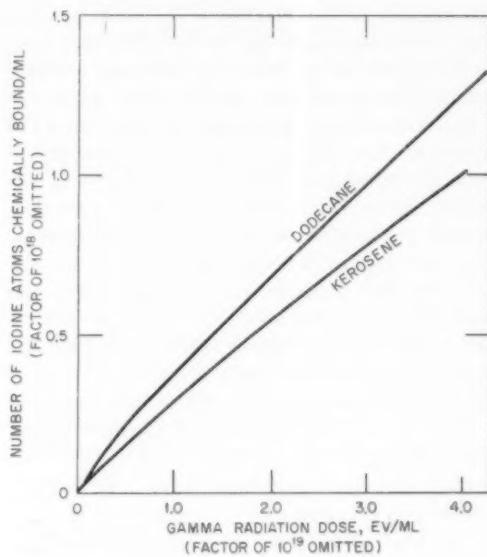
Figure 2—Comparison of irradiation-induced chemical bonding of iodine in Purex diluents dodecane and kerosene.[13]

Table IV-2 RADIATION DAMAGE TO VARIOUS SOLVENTS, DILUENTS, AND EXTRACTANTS[14]

Material irradiated	Radiolysis yield (G), molecules per 100 ev*		
	Gas	Monobasic acid	Dibasic acid
Amsco 125-82	1.45		
Solvesso-100	0.22		
TBP	1.28	2.09	0.18
D-s-BPP	0.55	0.79	
1M TBP in Amsco	1.38	0.72	0.19
1M D-s-BPP in Amsco	0.61	0.22	
1M TBP in Solvesso	0.30	0.25	0.03
1M D-s-BPP in Solvesso	0.30	0.19	

* All materials irradiated to 1.08×10^{22} ev per gram with 1-Mev electrons.

radiolytic gas yield from Amsco 125-82 was greater than that of Solvesso-100 by a factor of 5. In the case of the pure extractants, D-s-BPP was superior to TBP by a factor of 2 in radiation resistance. With diluent present, a beneficial effect was noted in the Solvesso-100 diluted TBP but not in the case of Solvesso-100 diluted D-s-BPP. Both Solvesso-100 and D-s-BPP are aromatic compounds. The authors suggested the possibility of a protective effect exerted by the benzenoid structure.[14]

Solutions of $1M$ D-s-BPP in Solvesso-100 were contacted with $1M$ or $0.03M$ nitric acid and irradiated to 45, 135, and 400 watt-hr/liter with 1-Mev electrons. Nitric acid extracted by the solvent was destroyed by relatively low levels of irradiation. G values (molecules of acid destroyed per 100 ev of radiation), for solvent equilibrated with $1M$ nitric acid, decreased from 2.88 to 0.97 as the irradiation dose was increased from 45 to 400 watt-hr/liter. Similar results were obtained for extractants equilibrated with $0.3M$ nitric acid. G values for the monobasic acid decomposition product of D-s-BPP decreased from 0.79 to 0.20 as the irradiation dose was increased from 45 to 400 watt-hr/liter for $1M$ D-s-BPP pre-equilibrated with $1.0M$ nitric acid.[6]

Other data are available bearing on the apparent superior radiation resistance of D-s-BPP and Solvesso-100. Data were obtained for the irradiation of $1M$ solutions of TBP, D-s-BPP, and di-n-butylphenyl phosphonate (D-n-BPP) in Solvesso-100. In the range of 10 to 300 watt-hr/liter irradiation, the production of organic acid had a linear dependence on dosage in the case of TBP. Nonlinearity was observed with the dialkylphenyl phosphonate. In subsequent zirconium-niobium extraction-scrubbing studies, satisfactory cleanup of all solvents was realized with a sodium carbonate wash followed by treatment with aluminum oxide.[8]

The experimental evidence thus far acquired indicates that, on the basis of radiation stability, Solvesso-100 is superior to kerosene as a Purex diluent. However, similar evidence of the resistance of Solvesso-100 to chemical degradation has not been reported. In addition, no reports of pilot-scale demonstrations with Solvesso-100 as the diluent have been published.

Plant and Equipment Design and Development

A terminal report[15] concerning the design of a Darex dissolution facility for enriched power-reactor fuel elements has been issued. The design drawings and specifications were about 75 per cent complete when the project was terminated. The terminal report emphasizes the phases of the mechanical design having general application to other Darex facilities. As a feed-preparation step, this plant would have batch-dissolved enriched, stainless-steel-clad power-reactor fuel elements in dilute aqua regia. The Darex process involves the dissolution of the fuel elements in hot aqua regia (5M nitric acid, 2M hydrochloric acid), concentrating and removing the hydrochloric acid from the product, clarification, and either storage or direct introduction into existing solvent-extraction facilities for radiochemical separation. The pilot-plant system included a dissolver column, evaporator, clarifier, scrubbers, storage vessels, and condensers, for a total of about 31 major pieces of equipment. About 16 were to be constructed of titanium, and most of the remainder, of type 304L stainless steel. These were arranged into nine units inside the cell and in three major service areas outside the cell.

Economical processing of spent reactor fuel elements by solvent extraction requires that the solvent be recycled. Prior to recycle, the solvent is washed with solutions such as aqueous sodium carbonate to remove fission products and solvent degradation products. A report concerning the capacity of a solvent washer suitable for use in a processing plant for enriched nuclear fuel has been issued.[16] On the basis of nuclear data from ORNL, the washer has "always safe" dimensions for partially reflected systems. The capacity of a critically safe washer, 7 in. in diameter by 9 ft 8 in. high, was determined for washing a solvent consisting of TBP dissolved in Ultrasene, a refined kerosene. The unit was operated satisfactorily at a solvent feed rate of 0.5 gal/min with a wash solution of $1M$ sodium carbonate. The tip speed of the paddle was 4.8 ft/sec, and the temperature was maintained at 90 to 100°F. The capacity for 6 per cent TBP-Ultrasene was only slightly greater than for 30 per cent TBP-Ultrasene. Increased temperature permitted operation at a higher paddle tip speed but at no increase in capacity. The feed rate could be increased to 0.9 gal/min by decreasing the paddle tip speed to 3.8 ft/sec, but only at a great sacrifice in the pumping capacity of the paddle and hence a postulated drop in washing efficiency. It was found necessary to maintain the aqueous liquid level above the shrouded paddle for satisfactory operation.

Ion-Exchange Processes

Recovery of Fission Products from Wastes

At ORNL, ion-exchange methods are being applied to the recovery of cesium and strontium from radioactive wastes.

A chelating resin, Dowex A-1, removed strontium from simulated neutralized Purex waste to which tartrate had been added to prevent iron precipitation.[6] Its strontium capacity was significantly higher at pH 7.5 than at 5.5, and at both pH's the capacity for rare earths was much lower than for strontium. Both strontium and rare earths were readily eluted with 2M nitric acid. The capacity for both strontium and rare earths was lower than that of a sulfonated cation-exchange resin, Dowex 50, but Dowex A-1 was easier to elute, and separation of strontium from rare earths was better.

In other studies at ORNL the addition, to 0.12M, of oxalic acid to 10-fold diluted simulated Purex first-cycle waste increased the 50 per cent breakthrough capacity of Dowex 50W-X8 resin for strontium from 7 to 22 resin-bed volumes and the 1 per cent breakthrough capacity for cerium from 16 to 67 volumes.[5] The increase results from complexing of iron in the feed, decreasing its competition for the resin. In a flow-sheet demonstration run, both strontium and cesium were loaded onto one Dowex 50 column; the strontium was eluted from this column and loaded on a second column with 1M nitric acid; the cesium was eluted from the first column with 0.5M citrate at pH 3.5, and the strontium was eluted from the second column with 0.07M EDTA at pH 6.1.

Cesium broke through at about 1500 resin-bed volumes when ORNL low-activity process waste was spiked with cesium and strontium tracers, made 0.01M in sodium hydroxide, filtered, and passed through Duolite C-3 (phenolic-sulfonic resin) or Duolite CS-100 (phenolic-carboxylic resin) at a rate of 600 volumes/day. Strontium breakthrough was significantly behind the cesium. More than 99.9 per cent of the activity was removed from the C-3 resin with 10 volumes of 5M hydrochloric acid, and from the CS-100 resin with 5 volumes of 2.5M hydrochloric acid, both upflow.

By a single bead contacting technique, the rate of uranyl sulfate loading on nitrate-equilibrated 1200-μ Dowex 21K was shown to be independent of the loading-solution sulfate concentration; it corresponded to an apparent uranium diffusion coefficient of 1.6×10^{-7} cm^2/sec, but results were scattered because of the nonuniformity of the beads. A new contactor that contacts several beads with a flowing solution under defined and reproducible hydrodynamic conditions consists of a submerged pump with a removable resin holder located at the pump outlet. Elution from 1200-μ Dowex 21K with neutral 1M sodium nitrate at a flow rate of 20 cm/sec gave results that fell near the curve predicted by an apparent uranium diffusion coefficient of 1.8×10^{-7} cm^2/sec.

Prior to initial criticality of the Shippingport pressurized-water reactor (PWR), development work was begun on the ion-exchange process associated with the waste-disposal system.[17] The PWR ion-exchange program showed that removal of Cs[137], Ba[140], Sr[90], Ce[144], Ru[106], Zr[95], I[131], and other radioisotopes from high-purity water can be accomplished by passage through mixed-bed ion-exchange columns in the hydrogen-hydroxyl form. Decontamination factors for these isotopes were found to average 10^3 across single 30-in. beds for processed volumes up to 7500 column volumes, and decontamination factors as high as 10^9 were observed for Sr[90].

The behavior, separation, and determination of many other elements are given in a literature survey by Cernak.[18]

Miscellaneous Ion-Exchange Studies

New types of ion-exchange equipment are being developed at Hanford. Preliminary studies of the operational stability and hydraulic characteristics of the multistage agitated-bed ion-exchange (MABIE) contactor have been completed.[19] Very stable operation has been demonstrated at all aqueous flow rates up to 450 gal/(hr)(sq ft) and at all resin flow rates up to 180 gal/(hr)(sq ft). The three-stage contactor reached stable hydraulic operation approximately 5 min after startup. In the one thorium transfer run for which analytical results are available, stage efficiencies of 80 per cent of theoretical (based on the resin residence time and an assumed diffusion coefficient of 4.4×10^{-8} cm^2/sec) were obtained at an aqueous flow rate of 290 gal(hr)(sq ft), a temperature of 35°C, and an aqueous-to-resin flow ratio of 20 liters/kg of dry resin. The waste loss from the three-stage contactor was 23 per cent. The operation was very stable throughout the run, as evidenced by the constancy of the raffinate analyses.

The significant results of the studies of the MABIE contactor are summarized below:[20]

1. A stage separator composed of sieve plates with 0.08-in.-diameter holes and 23 per cent free area provided good performance.

2. A 1-in.-diameter downcomer pipe, extending approximately 2 in. below the stage separator and nearly to the center of the column, provided adequate resin transport.

3. Good operation was demonstrated with the aqueous flow either upward or downward in the column.

4. The resin flow rate is independent of both agitation and aqueous flow rate.

5. A resin holdup of approximately 67 per cent of the contactor volume resulted in good operation with a minimum agitator power.

6. Operating under simulated adsorption-column conditions with a resin holdup of 67 per cent, the agitator speeds required to maintain steady state ranged from 400 to 800 rpm for aqueous flow rates ranging from 100 to 360 gal/(hr)(sq ft), respectively.

Based on the above data, an ion-exchange system has been designed consisting of an adsorption-scrub column operating with resin downflow and an elution column operating with resin upflow. Fabrication and installation of the column are approximately 75 per cent complete.

In the development of the Jiggler contactor discussed in previous Reviews,[21,22] hydraulic tests with Permutit SKB resin (10–20 mesh) indicate that the resin recycle capacity[20] of the $\frac{1}{2}$-in. recycle line is about 100 ml/min. The resin flow has been shown in recent tests to be unrelated to the amplitude-frequency product. The quantity of scrub acid required has been substantially reduced through addition of a separator in the air-lift resin recycle line.[23] Raising the level of the raffinate take-off line appears to be a reliable means of preventing the downflow of eluant from the strip column to the extraction column.

Two significant "flow-sheet" runs using thorium nitrate feeds have been completed since the changes described above were made. The first run at a feed rate of 500 ml/min appeared to have reached steady state with satisfactory thorium removal, namely, 97.7 per cent. However, the 2-ft-long strip column is apparently too short to effect the desired stripping. The feed rate, 900 ml/min, in the second run apparently was too great, and fluctuating recoveries of 20 to 90 per cent occurred.

Volatility Processes

The volatility of uranium hexafluoride is used as a basis for processing various types of ir-

radiated fuels. Developments are reported for several such processes noted below. One process, applied to uranium metal fuel, uses bromine trifluoride as a liquid fluorinating agent. Another liquid-phase process uses a fused-salt medium to carry out fluorination of high zirconium–uranium alloy fuel (which cannot be dissolved in liquid bromine trifluoride). Dry fluorination (solid-gas reaction) is applied to zirconium-uranium alloy fuel in one process involving fluorination of dried solid from a primary aqueous dissolution of zirconium alloy fuel, and in another process using direct hydrofluorination of the alloy (with a hydrogen chloride catalyst) followed by a fluorination step. Hydrochlorination of the zirconium-uranium alloy is also used to volatilize zirconium chloride prior to fluorination of the uranium residue. A direct fluorination process has been applied to uranium dioxide fuels. Fluidization techniques have been involved in these dry halogenation processes to enhance process control. Application of fluoride-volatility techniques to the processing of plutonium-bearing fuel is also being studied.

Dissolution of Uranium
in Liquid Bromine Trifluoride

In the bromine trifluoride process for recovery of uranium hexafluoride from uranium metal fuel elements, fluorination is carried out in a liquid phase of bromine trifluoride. Demonstration of this process has been carried out in laboratory and pilot-plant studies.[24,25] However, a pilot-plant explosion in 1957 during a dissolution experiment[26] has led to a study of ignition of metallic uranium in this medium. Previous work has been reported.[27]

Studies at Brookhaven National Laboratory (BNL) on the ignition and detonation of uranium in bromine trifluoride solutions were continued by using uranium turnings to simulate the porous interior of a nearly dissolved BNL slug. Ignitions were obtained after dissolution for as much as 17 min at 145°C, and detonations were obtained after dissolution for 45 sec at 123°C. High-speed moving pictures have shown that, although ignition may start in some cases where the uranium turnings are partially immersed in liquid, detonation does not occur until immersion is complete.[28]

Several forms of uranium cylinders, machined from the center of a BNL slug, were

tested for ignition while undergoing dissolution. A hollow cylinder containing small flat pieces of uranium was used to simulate the poor heat-removal condition and surface area which conceivably could exist inside a dissolving BNL slug; ignition followed 18 sec after immersion in solution[28] at 131°C.

The manner of dissolution of BNL and Hanford uranium was observed in a series of runs. Severe pitting was found with these specimens, but cast uranium dissolved without pitting. The specific area of the BNL specimen increased by a factor of 6 and reached an area equivalent to that of the small pieces which ignited in the hollow uranium cylinder. However, the ignition or detonation of a nearly dissolved BNL uranium slug has not yet been observed.[28]

Fused-Salt Processing

In the fused-salt process for recovery of uranium from zirconium-matrix alloy fuels, the alloy is dissolved in a molten fluoride mixture with a hydrogen fluoride sparge and then uranium hexafluoride is volatilized with a fluorine sparge.[24,25]

Corrosion of metal vessels has been a matter of concern with this process. One effort to eliminate corrosion in the primary step has been to use a graphite dissolver, which is undergoing tests.

A series of four complete dissolutions was carried out semicontinuously in the graphite pilot-plant dissolver at ANL according to the fused-salt fluoride-volatility process flow sheet. In this process the uranium-zirconium alloy fuel was dissolved in the molten fluoride salt mixture at 600 to 700°C with a hydrogen fluoride sparge. Partial salt transfers and salt makeup were carried out between dissolutions. The salt mixture was between 40 and 50 mole % zirconium fluoride. Dissolution rates of up to 2.3 mg/(cm^2)(min) or about 9 mils/hr were obtained. The zirconium-uranium 10-plate fuel elements were carried to 90 per cent dissolution in as little as 6 hr. Graphite heaters and other components functioned satisfactorily.[29]

At ORNL, pilot-plant studies of the dissolution of synthetic Zircaloy-2 plate type elements in lithium fluoride – sodium fluoride – zirconium fluoride salt were carried out in an INOR-8 dissolver. In one run a test element was hydrofluorinated to about 50 per cent weight loss at an average rate of 1.5 mg/(cm^2)(min), and the

fused salt was discharged and cooled. A heavy layer of metallic contaminants found on the fuel element in the salt phase contained visible amounts of dark-colored contaminants. After recharging was done, the dissolution was resumed and a normal rate of 0.7 mg/(cm^2)(min) was found. A sharp end point was indicated by a greatly decreased hydrogen evolution, and both salt and vessel were relatively clean and free of contaminants with no test element remaining. Previous reports of heavy corrosion-product accumulations were based on runs stopped short of completion. It appears that corrosion products are dissolved at the end of the zirconium dissolution.[30]

In the other runs carried to completion, over-all dissolution rates of 1.0 and 1.5 mg/(cm^2)(min) were obtained at temperatures of 550 and 650°C, respectively. Initial salt compositions were about 34 mole % and 18 mole % zirconium fluoride, respectively. Metal occlusions in salt slag were noted in some cases.[31]

In two engineering-scale runs, Zircaloy-2 dissolved in 43 mole % sodium fluoride – 57 mole % lithium fluoride melts (using a copper-lined dissolver to minimize contamination from corrosion products) at average rates which changed from 0.46 to 0.27 lb/(hr)(sq ft) as the zirconium tetrafluoride concentration of the melt was increased[5] from 0 to 45 mole %.

Development of the fused-salt process has been directed chiefly toward zirconium-matrix fuels. However, laboratory-scale tests of other materials for possible process application have been made. The dissolution of niobium, stainless steel, and thoria by hydrofluorination in fused fluorides was investigated. In the presence of hydrogen fluoride, niobium metal dissolved at rates of 1 to 3 mg/(cm^2)(min) in 31 – 24 – 45 mole % lithium fluoride – sodium fluoride – zirconium fluoride at 600°C, respectively. In one test with 42.0 – 45.5 – 11.5 mole % potassium fluoride – lithium fluoride – sodium fluoride, the stainless-steel dissolution rate[6] was about 4 mg/(cm^2)(min) at 600°C.

Thoria pellets (1750°C fired) reacted relatively slowly with gaseous hydrogen fluoride in a 57 – 43 mole % lithium fluoride – sodium fluoride melt, at a dissolution rate of only 0.3 mg/(cm^2)(min) at 700°C. The same pellets and arc-melted thoria dissolved completely in 5 to 10 min in 31 – 24 – 45 mole % lithium fluoride – sodium fluoride – zirconium fluoride salt at

650°C without the use of hydrogen fluoride. The resulting oxyfluoride solution was hydrofluorinated or directly fluorinated rapidly.

Molybdenum, at a concentration of several thousand parts per million, was the major contaminant in the uranium hexafluoride product of the volatility process in laboratory-scale tests with USS *Nautilus* fuel. Although molybdenum hexafluoride behaved similarly to uranium hexafluoride in the sodium fluoride absorption-desorption process, the similarity does not appear to be so great that they cannot be separated. Preliminary data from a chemical investigation of the molybdenum hexafluoride—sodium fluoride system indicated that the complex is $MoF_6 \cdot 3NaF$ and that the equilibrium partial pressure at 25°C is >1 mm; whereas the equilibrium partial pressure for uranium hexafluoride is $\sim 10^{-6}$ mm in the sodium fluoride—uranium hexafluoride system.[6]

In laboratory studies carried out in a radioactive cell with *Nautilus* fuel, molybdenum, technetium, neptunium, and chromium were the chief contaminants of the uranium hexafluoride product. There was no plutonium in the product. The molybdenum varied from 1250 to 10,100 ppm, and the technetium from 56 to 1020 ppm, based on uranium. The chromium contamination may have arisen in hydrolysis of the uranium hexafluoride in a stainless-steel vessel. The presence of the first three indicates that they behave similarly to the uranium hexafluoride in the sorption-desorption process. The first sodium fluoride bed contained some plutonium but no neptunium; 5 per cent of the neptunium was removed from the product stream by the second sodium fluoride bed. Small differences in fluoride flow rates or temperatures are believed to account for the molybdenum and technetium variations. Vapor pressure measurements of the molybdenum hexafluoride—sodium fluoride complex indicate that its decomposition temperature is 125°C (at 760 mm) and that absorption of uranium hexafluoride on sodium fluoride above this temperature would lead to a marked decrease in molybdenum contamination of the uranium hexafluoride.[5]

Fluorination Processes

Other schemes involving the volatility of uranium hexafluoride for processing irradiated fuels are under study at ANL. These include the aqueous dissolution dry fluorination (ADF) process and a direct fluorination process.[29]

In the development of the ADF process, current emphasis is being directed toward recovery of uranium from low uranium—Zircaloy-2 fuel alloys. Major process steps are aqueous dissolution of the fuel, fluid-bed drying of the solution to a dry powder, and fluorination of the powder to remove and recover the uranium as the hexafluoride. The use of additional anhydrous hydrogen fluoride as part of the fluidizing gas during drying did not lower the residual oxygen and water content of the dryer products, whereas a separate hydrofluorination step carried out at slightly higher temperatures (450°C) eliminated about two-thirds of these components. A jet-target grinder capable of higher attrition rates than the ordinary attrition jets was successful in stabilizing the particle-size distribution during the recent dryer studies.[29]

A new 2-in.-diameter 6-ft-tall static-bed fluorination reactor was installed and operated to gain additional information on the effects of powder (cake) depth on fluorine efficiency and pressure drop.

Exploratory experiments on alternate non-aqueous schemes for processing low uranium—zirconium alloy fuels were made. Encouraging results were obtained upon fluorination of a hydrided and hydrofluorinated specimen of 1.4 per cent uranium-zirconium alloy. Hydriding of the 3.3-g specimen was carried out at 825°C in a 5-psig hydrogen atmosphere for an overnight period ($\sim$14 hr). The hydride was degraded to a fine powder (-200 mesh) in only 1 min in a mechanical mortar, and a portion of this material was then hydrofluorinated at temperatures to 450°C and fluorinated at 700°C on a thermobalance. The uranium content of the residue after this treatment was only 0.01 per cent.[29]

The direct fluorination process is currently aimed toward the processing of the Zircaloy-clad, uranium dioxide fuel typical of the Dresden reactor. This process involves direct fluorination of oxide matrix with fluorine or other fluorination agents to produce volatile uranium hexafluoride and plutonium hexafluoride. Laboratory-scale equipment has been constructed from which information can be obtained to substantiate a process flow sheet in regard to plutonium hexafluoride transfer, fluorination of uranium and plutonium oxide mixtures, and separation of uranium and plutonium hexafluo-

rides. The use of sulfur tetrafluoride as the fluorinating agent is being investigated in reactions with uranium tetrafluoride, uranium dioxide, U_3O_8, uranium trioxide, uranyl fluoride, plutonium dioxide, and plutonium tetrafluoride.[29]

Several approaches are being considered to achieve process separation of the hexafluorides of uranium and plutonium. One approach to the separation of this hexafluoride utilizes the preferential reduction of the more chemically reactive plutonium hexafluoride by sulfur tetrafluoride. Another separation is based on the relatively lower stability of plutonium hexafluoride, for which the equilibrium dissociation $PuF_6 \rightleftharpoons PuF_4(s) + F_2(g)$ tends[32] strongly to the right:

$$K_p = \frac{P_{F_2}}{P_{PuF_6}} \doteq 400 \text{ at } 300°C$$

A third approach is that utilizing the relatively higher rate of production of uranium hexafluoride from the fluorination of mixtures of the tetrafluorides of uranium and plutonium. In laboratory "boat-reactor" experiments, approximately 85 per cent of the uranium was volatilized without any substantial loss of plutonium from the residue. After further fluorination, less than 1 per cent of the plutonium remained in the residue.[32]

In pilot-plant-scale tests, the direct fluorination of dense uranium dioxide pellets submerged in an inert fluidized medium was carried out in a 3-in. reactor at 500°C at fluorine concentrations up to 30 per cent. Negligible fines were produced with a 3-in. pellet bed under the conditions used, although substantial amounts of fines were found in deeper beds. Uranyl fluoride was identified as the major species in the fines. The reaction rate was found to be directly proportional to fluorine concentration and ranged from 102 to 119 lb of uranium hexafluoride/(hr)(sq ft of reactor cross section)(atm fluorine) in these tests. The concentration of unreacted fluorine in the off-gas decreased approximately exponentially with bed height, with a corresponding increase in the over-all fluorine efficiency. Fluorine efficiency of well over 90 per cent was obtained in a 9-in. bed. The formation of small amounts of solid intermediate uranium compounds was observed[29] in the case of pellet beds deeper than 3 in.

Experimental work has continued at ANL to determine the mechanism of the nickel-fluorine reaction. As a means of checking the validity of the experimental method, both oxidation and fluorination reactions have been used. The results indicate that the mechanism for the nickel-fluorine reaction is one in which fluorine migrates through the nickel-fluorine film.

An Oak Ridge Gaseous Diffusion Plant study on the high-temperature corrosion of nickel and refractories by fluorine and uranium hexafluoride was reported in an earlier Review.[21] An unclassified version of this report has recently been released.[33] Some studies not reported earlier are presented here. Samples of fused alpha alumina, alpha alumina–magnesium oxide spinel, and alpha alumina–nickel oxide–nickel cermet were exposed to undiluted fluorine at 1 atm absolute pressure at temperatures of 1340 and 1500°F. By visual observations the samples retained their original shape and showed no evidence of a nonuniform attack. Conversion of the sample surfaces to the respective metal fluorides was ascertained by X-ray diffraction patterns of the films. From the weight gain of the alpha alumina during the 1340°F fluorine exposure, a rather arbitrary comparison based on the average depths of penetration indicated that the alpha alumina is as good as the nickel in the region of 1300°F and is worthy of further consideration.

Grade A nickel samples coated with nickel fluoride films of 37,000 and 74,000 A, respectively, were exposed to an absolute pressure of gaseous uranium hexafluoride of 12 cm Hg at temperatures of 1500 and 1800°F. The initial uranium hexafluoride consumption rates at 1500 and 1800°F were of the order of 700 and 800 mg of uranium/(sq ft)(day), respectively. Both nickel fluoride and uranium tetrafluoride corrosion products have appreciable vapor pressures at these test temperatures, and they were observed to migrate to the cooler portions of the reactor by vapor-phase transfer. The average penetration of the nickel by the uranium hexafluoride at 1500°F, as calculated from the average nickel fluoride scale, is quite similar to that experienced in the exposures to fluorine.

Observations indicate that after passage of an initial period during which a relatively low corrosion rate in uranium hexafluoride at 1800°F is experienced, nickel is attacked at an accelerated rate with the resultant deposition of large quantities of uranium tetrafluoride.

Thus the use of nickel to contain uranium hexafluoride or fluorine at 1800°F is not promising owing to the volatility and instability of the nickel fluoride, the intergranular attack of the metal, and the proximity to the melting point of nickel, 2647°F.

A procedure for studying absorption kinetics involving temperature measurements in an adiabatic differential reactor was developed at ORNL.[34] The method was tested for the absorption of hydrogen fluoride from a nitrogen stream on sodium fluoride pellets. The method was applied to a study of the kinetics of the absorption of uranium hexafluoride from nitrogen onto sodium fluoride.

It was concluded from the experimental results that:

1. Temperature measurements in an adiabatic differential reactor provide a quick, practical method of measuring absorption rates for uranium hexafluoride and hydrogen fluoride on sodium fluoride pellets.

2. For mixtures of uranium hexafluoride (12 mole% and less) and nitrogen at initial temperatures from 70 to 105°C, the absorption rate of $\frac{1}{8}$ in. right cylindrical sodium fluoride pellets drops close to zero after about 5 min. During the first 2 min of exposure, the absorption rate builds up rapidly to a peak and then declines sharply. In this region the rate depends strongly on both temperature and uranium hexafluoride concentration. The present study does not yield a rate-controlling mechanism during this period. During the last 3 min the rate declines slowly to zero and depends little on temperature, concentration of uranium hexafluoride in the gas stream, or mass velocity of the stream. This behavior suggests an internal diffusion mechanism for this part of the process.

Some recently declassified data on the preparation and properties of plutonium hexafluoride are reviewed in a Knolls Atomic Power Laboratory (KAPL) paper.[35] Studies of the rate of decomposition of plutonium hexafluoride on stressed aluminum are reported. This precedes the more recent work done at ANL on plutonium hexafluoride decomposition.

Dry Halogenation Processes

The name "volatility processes" has traditionally been used to refer to fluoride-volatility separation schemes. However, separation methods based on the volatility of compounds other than the fluorides have also been studied. Notable among these is the separation of zirconium from uranium by volatilization of zirconium tetrachloride. This process is under development as a head-end step in which the separated uranium is used as feed to a final decontamination process. The latter process may be either solvent extraction, in the case of the ORNL Zircex process, or fluoride volatility, in the case of the BNL fluid-bed process. A variation of these schemes under study at ANL involves hydrofluorination of the zirconium, using hydrogen chloride as catalyst, followed by fluorination of the solid products to volatilize uranium.

The Zircex process is based on the use of hydrogen chloride gas at temperatures of 350 to 800°C to convert various uranium-zirconium alloys to volatile zirconium chloride and relatively nonvolatile uranium trichloride. After hydrochlorination is complete, the uranium chloride is dissolved in nitric acid. Chloride removal and feed-adjustment operations are then employed to produce a solvent-extraction feed solution which contains little of the original zirconium structural material. Six major problems have prevented the immediate use of the Zircex process as a means of processing spent nuclear fuel alloys:

1. Removal of the heat generated in the exothermic gas-solid reactions.

2. Uranium loss to the zirconium tetrachloride sublimate.

3. Design of a satisfactory method of removing zirconium tetrachloride from the hydrochlorination off-gas stream.

4. Uranium loss to a nitric acid—insoluble hydrochlorination residue in the case of high zirconium—uranium alloy type fuel.

5. Corrosion in the hydrochlorinator caused by cyclic use of hydrogen chloride gas at 350 to 800°C and boiling nitric acid.

6. The possibility of explosive reactions resulting from the contact of nitric acid with uranium-zirconium alloy, should hydrochlorination be incomplete.

These problems are interrelated, and the solution of one problem tends to change the importance of others. The problem of heat removal decreased in importance when it was discovered that uranium chlorides could be easily removed from the off-gas stream. This discovery permitted use of much higher reac-

tion temperatures and also permitted reduction of the uranium loss to the zirconium tetrachloride sublimate to tolerable levels. In runs in which the inside of the fuel element reached temperatures of 900°C, no damage to the hydrochlorinator was observed. Further engineering work has been directed toward development of a satisfactory desublimer for zirconium tetrachloride.[36]

The use of carbon tetrachloride in a modified Zircex flow sheet promises improvements simultaneously in items 4, 5, and 6 above. The carbon tetrachloride successfully chlorinates residual oxides which previously resulted in losses, and sublimation of uranium chloride avoids the necessity of contacting the hydrochlorinator with nitric acid, thus lowering corrosion on this major piece of process equipment.[36] In the revised Zircex flow sheet, uranium-zirconium fuels are first hydrochlorinated at ~500°C, which removes most of the zirconium as the volatile tetrachloride. The residual zirconium oxide−uranium trichloride is then contacted with a gaseous carbon tetrachloride−oxygen mixture to produce volatile zirconium and uranium tetrachlorides. In a Zircex run in which all the hydrochlorination residue was converted to volatile chlorides by reaction with carbon tetrachloride, less than 0.01 per cent of the uranium from a 7 per cent uranium−zirconium alloy sample was lost. The uranium desublimer was packed with copper turnings.[29] When nickel turnings were used

only one-third of the rate at 600°C. No reaction was evident below about 500°C with high-uranium residues obtained from hydrochlorination of low-zirconium alloy fuel.[37]

Pilot-plant-scale development at BNL continued on a fluid-bed hydrochlorination of zirconium-matrix fuels. In this process volatile zirconium tetrachloride is formed as a first step. A second step involves fluorination of the nonvolatile uranium chloride residue to form uranium hexafluoride products.

Subsequent to earlier reports[22,38] that described initial hydrochlorination runs in which 7 kg of Zircaloy-uranium plate fuel elements were reacted, it was found that only 0.4 per cent of the uranium passed out of the reactor into the off-gas absorbing tank. In these early runs, central plate temperatures in the 26-plate element were as much as 400°C over the fluidized-bed temperature. This indicated a lack of fluidization in the internal areas between the plates of the elements, which in turn was probably due to a combination of the close (45 mil) plate spacing and the relatively large particle size of the sand used as the fluid bed (60 to 80 mesh). The sand was replaced with a bed of stainless-steel powder in the size range 140 to 200 mesh. The higher density of the stainless steel compensates to some extent for the smaller particle size, allowing the use of fluidizing-gas velocities comparable to those with the sand bed. Data on Runs 10 through 14 are shown in Table IV-3. At a high reaction

Table IV-3   PILOT-PLANT HYDROCHLORINATION OF ZIRCALOY-URANIUM FUEL PLATES[40]

Run No.	Initial weight, g	Elapsed time, min	Bed temp., °C	Vol.% HCl	Reaction rate, mils/hr	Max. plate temp., °C	HCl utilization, %	Weight loss, g
10	6900	6	440−460	100	18.5	480		330
11	6570	21	430−470	59−75	10.5	480	22	640
12	5930	13	430−470	100	14.1	490	21	540
13	5390	32	470−535	100	36.9	560	40	2733
14	2657	40	470−535	100				~2500

as de-entrainment packing for the uranium chloride condenser, >10 per cent of the uranium was lost to the zirconium chloride condensate.[6]

Nitric acid−insoluble residues of zirconium-uranium oxides obtained from the hydrochlorination of high-zirconium fuel samples were chlorinated with carbon tetrachloride in an inert carrier gas. The reaction rate at 350°C was

rate of 37 mils/hr, maximum plate temperatures were only about 20°C above the temperature of the bed. Attack of the plates was uniform over the length of the element. The reaction was carried to completion with no adverse effects with regard to fluidization characteristics of temperature control. After the reaction, only a few small flakes were found resting on the support grid.[39]

Nickel powder was considered as a fluid-bed medium for a fluorination step. In a laboratory test no detectable uranium remained after hydrochlorination followed by fluorination with excess fluorine. However, nickel powder was found to cake sufficiently during hydrochlorination to stop fluidization. A laboratory screening has been initiated[40] on materials which are compatible with hydrogen chloride and fluorine and which may be suitable as a fluid-bed medium.

Experimental work has started at ANL on the direct hydrofluorination of Zircaloy coupons using anhydrous hydrogen fluoride and mixtures of hydrogen fluoride—hydrogen chloride gas with an inert fluidized bed as heat-transfer medium. This work has application to both Zircaloy-clad and uranium-Zircaloy alloy fuels where the uranium (and plutonium) would be made available for processing via fluoride-volatility schemes.[29] In this process the hydrogen chloride apparently acts as a catalyst to promote the formation of nonvolatile zirconium tetrafluoride, which is then handled as a solid effluent.

Initial experiments have been carried out in a $1\frac{1}{2}$-in.-diameter reactor using calcium fluoride as the inert fluidized medium. The data are summarized in Table IV-4. Temperatures

Table IV-4   DIRECT HYDROFLUORINATION* OF ZIRCALOY USING HYDROGEN CHLORIDE CATALYST[29]

| Temp., °C | Run dura-tion, hr | Nominal inlet gas composition | | Weight loss of coupon, % | Average penetra-tion rate, mils/hr |
		HF, vol.%	HCl, vol.%		
525	7	100	0	52.2	~1.6
540	4	89	11	100	>15
450	4	95	5	84	~5

* Carried out in a $1\frac{1}{2}$-in.-diameter reactor using CaF_2 as the inert fluidized medium.

of 450 to 540°C were used with gas streams of the following compositions: 0 and 100, 5 and 95, and 11 and 89 vol.% for the hydrogen chloride and hydrogen fluoride concentrations, respectively. The Zircaloy specimens were prepared with an oxide coating by autoclaving in steam for four days at 350°C to simulate the film formed on the fuel plates in a nuclear reactor. The anhydrous hydrogen fluoride at 525°C produced a modest penetration rate of about 1.6 mils/hr, whereas the addition of only 5 vol.%

hydrogen chloride at 450°C resulted in at least a 5 mils/hr rate. The rate of intergranular attack was probably higher in the latter case since the specimen was found broken into three sections at the end of the run. The most severe conditions tried, 11 vol.% hydrogen chloride at 540°C, resulted in complete disintegration of the sample in 4 hr and gave a penetration rate[29] in excess of 15 mils/hr.

Physical Properties of Halogens
and Halogen Compounds

An excellent review article on the physical properties of the halogen fluorides has been written by Rogers.[41] It includes the work done by Rogers and coworkers at Michigan State University. Some of the physical properties of the pure halogen fluorides, as well as certain of their solutions, have been interpreted in terms of ionization, association, and electron donor-acceptor properties of these molecules. The author speaks of the association in liquid bromine trifluoride and iodine pentafluoride in terms of fluorine bridges. This is a phenomenon akin to hydrogen bonding and probably plays an important part in the structure of halogen fluoride liquids.

A ternary diagram (H^+, F^-, and Zr) was developed at Phillips Petroleum Co., Atomic Energy Division,[42] to provide a systematic approach to the preparation and interconversion of three sodium fluozirconates ($2NaF \cdot ZrF_4$, $3NaF \cdot ZrF_4$, and $5NaF \cdot 2ZrF_4 \cdot HF$) in low-acid, low-fluoride, zirconyl systems. Evidence is presented for the formation of a $ZrOF^+$ ion.

Pyrometallurgical Processing

Because of their potential in simplifying the fuel cycle and in effecting a consequent reduction of processing costs, development of pyrometallurgical processes is being pursued at several atomic energy sites. These are processes in which the fuel is retained in the metallic state throughout or is produced as an intrinsic characteristic of the process, e.g., molten-salt electrolysis. The processes are, in general, not high-decontamination processes, and their development must, therefore, be paralleled by the development of remote fuel refabrication procedures. In a recent article[39] pyrometallurgical processes are discussed

along with other processes in use or under investigation in the United States.

Many of the procedures being investigated for metallic fuels are applicable to ceramic fuels (fission-product volatilization, fused-salt extraction or electrolysis, and oxidation-reduction reactions). These applications are also discussed in the section.

Much of the work and information in this field is general in nature, being developed to provide the necessary background information for process selection. However, melt refining and other pyrometallurgical processes are under development for specific purposes in the fuel cycle of Argonne's EBR-II, now under construction at Arco, Idaho. Discharged fuel from this reactor will be processed by pyrometallurgical methods in an adjacent fuel-processing plant. This will constitute the first large-scale demonstration of pyrometallurgical methods.

Construction of the fuel-cycle facility at Arco, Idaho, is about 20 per cent complete.[43] Construction of an adjacent laboratory and service building has been essentially completed. A record of the development and demonstration of the specialized equipment for the fuel-cycle facility is provided in quarterly reports[43] of the ANL Chemical Engineering Division, the latest being ANL-6183.

Melt Refining

The EBR-II cycle is shown in Fig. 3. The first process to be employed in the EBR-II processing plant is melt refining, a process which consists simply of melting the fuel in a stabilized zirconium oxide crucible and holding it molten for several hours at a temperature of 1400°C prior to pouring it into an ingot. During this time, removal of fission products is effected primarily by selective oxidation and volatilization. Liquid-metal processes are currently under development for reclaiming the fissionable material in the crucible skull.

The entire first fuel loading of the EBR-II is being prepared by the processes and techniques to be employed in the EBR-II processing plant. This is being done to provide information on equipment performance in long-term and repetitive operations, to expose flaws in operating techniques and equipment design, and to train personnel in the required remote operations. Some difficulties were recently encountered as a result of cracking of the zirconia crucibles.[43]
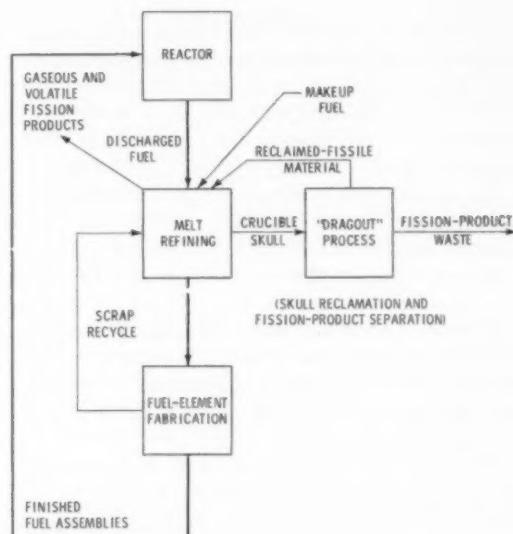
Figure 3—EBR-II fuel cycle (J. H. Schraidt, ANL, private communication).

These have been largely eliminated by reducing temperature gradients in the crucible wall and by closer quality control by the manufacturer of the crucibles.

Other improvements in the melt-refining furnace have been effected through better high-temperature insulation and development of more efficient traps for collecting sodium and other fission-product condensable vapors which are evolved in the melt-refining operation.

Oxide slagging (often used synonymously with melt refining except that the latter also includes other purification reactions such as volatilization) and halide slagging have been studied as methods of fission-product removal from plutonium reactor fuels.[44] Synthetic fission-product alloys were prepared by dissolving selected key fission-product elements in a base fuel alloy (10 at.% iron in plutonium, melting point 406°C). The fission-product concentrations corresponded to those calculated for 10 per cent burnup of the fuel. In some cases this alloy was used directly, but in others it was liquated at 600°C for a prolonged period and filtered, which removed insoluble solid phases involving the fission-product elements, zirconium, molybdenum, and lanthanum. The compositions of the original fissium and the liquated alloys were as follows:

Element	Concentration, wt.%	
	Original alloy	Liquated alloy
Pu	91.47	95.21
Fe	2.56	2.54
Zr	0.81	<0.003
Mo	0.87	0.036
Ru	1.31	1.22
Ce	1.05	0.75
La	1.93	0.24

As with the EBR-II melt-refining process, a temperature of around 1400°C was required to realize reasonable rates of removal of cerium and lanthanum in zirconia (see Table IV-5) or

Table IV-5   EFFECT OF SLAGGING TEMPERATURE ON PURIFICATION OF FISSIUM ALLOY AND RECOVERY OF PLUTONIUM IN ZIRCONIA CRUCIBLES[44]

Temp., °C	C/C_0 (final concentration/ original concentration)						Pu recovery, %
	Fe	Zr	Mo	Ru	Ce	La	
1000	1.01	1.00	1.04	1.01	0.99	0.97	99
1200	0.99	0.99	0.96	1.00	0.79	0.46	95
1400	1.02	0.98	1.09	0.99	0.39	0.03	91

magnesia crucibles. A study of the effect of time shown in Table IV-6 indicates that zirconia removes lanthanum more rapidly than does magnesia but that removal of cerium is slow in both materials.

Table IV-6   EFFECT OF SLAGGING TIME AT 1400°C ON PURIFICATION OF FISSIUM ALLOY AND RECOVERY OF PLUTONIUM[44]

(Scale: 1 kg)

Time, hr	C/C_0 (final concentration/ original concentration)						Pu recovery, %
	Fe	Zr	Mo	Ru	Ce	La	
2*	1.00	0.98	0.95	1.03	0.63	0.16	93
4*	1.02	0.98	1.09	0.99	0.39	0.03	91
2†	0.90	0.93	0.95	1.01	0.57	0.40	>91
5†	1.02	0.98	0.98	1.07	0.40	0.13	93
8.3†	1.02	0.81	0.85	1.00	<0.006	<0.001	72

* In a zirconia crucible.
† In a magnesia crucible.

Halide slagging by slags of various compositions was conducted in tantalum crucibles at temperatures of 600 to 700°C. Results with a eutectic plutonium trichloride – sodium chloride

salt presented in Table IV-7 show complete removal of cerium and lanthanum. By virtue of the reaction $PuCl_3(salt) + La(metal) \rightarrow LaCl_3(salt) + Pu(metal)$, this salt also serves

Table IV-7   REMOVAL[44] OF FISSION-PRODUCT ELEMENTS FROM LIQUATED PLUTONIUM FISSIUM BY $PuCl_3$-NaCl SLAG AT 600°C

(Started with 100.4 g of alloy and 32.45 g of salt)

Equilibration time, hr	C/C_0 (final concentration/ original concentration)				
	Fe	Mo	Ru	Ce	La
3	0.93	1.0	0.96	<0.009	<0.04
6	0.94	0.9	0.99	<0.01	<0.04
30	0.97	0.9	0.94	<0.01	<0.04

as a fuel-replenishing step. Magnesium chloride used instead of plutonium chloride as the slagging agent (in a magnesium chloride – potassium chloride – sodium chloride slag) gave equally good removal of cerium and lanthanum, these removals occurring within an hour (Table IV-8). A 10 per cent excess of magnesium

Table IV-8   REMOVAL[44] OF FISSION-PRODUCT ELEMENTS FROM LIQUATED PLUTONIUM FISSIUM BY $MgCl_2$-KCl-LiCl SLAG AT 600°C

(Started with 99.7 g of alloy and 12.88 g of slag)

Equilibration time, hr	C/C_0 (final concentration/ original concentration)				
	Fe	Mo	Ru	Ce	La
1	0.98	1.0	1.01	<0.01	<0.03
2.5				<0.01	<0.03

chloride did not cause an excessive plutonium loss, plutonium recovery still being 99 per cent. Results in both cases were in agreement with theoretical calculations. Equally good results were obtained with a magnesium chloride – sodium chloride – potassium chloride slag at 700°C.

The high temperatures and slow reaction rates were concluded to be serious disadvantages of oxide slagging achieved by a solid-liquid reaction. In contrast, liquid-liquid reactions between molten fused-salt and metal phases were considerably more rapid. The kinetics of reactions between liquid metals and liquid salts is under study by the Department of Metallurgy at Massachusetts Institute of Tech-

nology, and progress reports have recently been issued.[45,46]

Fundamental Studies. The free energies of formation of uranium, molybdenum, and tungsten trioxides have recently been reported by Ackerman and coworkers.[47] The heats of formation of plutonium dioxide and U_3O_8 have been determined by Popov and Ivanov.[48] A system composed of the dioxides of uranium, thorium, and zirconium has been studied at elevated temperatures (up to 1400°C) in a hydrogen atmosphere. The zirconia can dissolve about 8 mole % uranium dioxide.

The formation and properties of cerium tellurides have been investigated by Domange and coworkers of France.[49] One of the postulated mechanisms for the simultaneous removal of tellurium and cerium from molten uranium during melt refining is through formation of cerium tellurides.

Liquid Metal and Salt Processes

Pyrometallurgical processes which employ liquid metals as processing media are being developed at several sites. These generally involve zinc, cadmium, magnesium, mercury, aluminum, and bismuth as solvent metals. The chemistry of the various liquid-metal systems is being investigated to provide basic data and concepts for the logical design of separations processes. These processes generally include dissolution in a suitable liquid-metal solvent, fractional crystallization or extraction by fused salts or immiscible liquid metals to provide the desired separations, and product recovery by vaporization of the solvent metal.

Solubility data have been reported for the following: (1) titanium, praseodymium, neodymium, and uranium in cadmium, (2) uranium in liquid lead over the temperature interval[43] 415 to 802°C, (3) uranium in molten aluminum alloys as a function of temperature and zinc and molybdenum concentrations,[50] and (4) uranium as a function of magnesium concentration in cadmium-magnesium solutions[43] at 610°C. In the latter system, the uranium concentration decreased smoothly from 2 per cent in pure cadmium to 0.002 per cent in a 72 per cent magnesium—cadmium system. In many of the above systems, the equilibrium solid phase has been characterized. Standard free energy, enthalpy, and entropy of formation data have been determined from zinc vapor pressure measurements for intermetallic compounds in the zinc-zirconium and zinc-uranium systems.[51] Relations for vapor pressure and free energy are presented as a function of temperature. The identification of the intermetallic phases in the ruthenium-zinc and uranium-cadmium systems is in progress at the Bureau of Standards.[52]

The partition coefficients have been measured[43] for several fissile and fission-product elements between the immiscible metals, aluminum and cadmium, at 680 to 688°C. Values of the coefficients (weight per cent in aluminum phase/weight per cent in cadmium phase) are: uranium, 1.45×10^5; palladium, 5800; cerium, 170; praseodymium, 160; lanthanum, 46; and zirconium, 82. The distribution of samarium between uranium-chromium and magnesium-silver eutectic at 1000°C has been reported[53] to be highly in favor of the magnesium phase with a distribution coefficient of 30,000 to 40,000. A study of the distribution of silver between lead and zinc has recently been published[54] along with other derived thermodynamic data. The silver strongly favors the zinc phase. This is the basis of the well-known Parks process for removal of silver from lead.

Progress continues to be made at ANL on the reclamation process for fissionable material contained in the crucible residues after a melt-refining operation. The flow sheet given in Fig. 4 illustrates a proposed process which begins with reduction in pure magnesium.[43] The fission-product separation steps are based upon solubility and concentration differences between uranium and the various fission-product elements. The process is arranged so that uranium precipitations are made from two different liquid-metal media in order to take advantage of different fission-product behavior in these two media. The two liquid-metal media are a magnesium-rich solution, from which uranium precipitates as metal, and a zinc-rich solution, from which uranium is precipitated as an intermetallic compound, U_2Zn_{17}.

Two flow-sheet runs have been made to demonstrate that the process steps could be performed and to pinpoint problems. Recovery of uranium in the skull oxidation step exceeded 99 per cent. The introduction of zirconia-crucible fragments was less than 2 per cent of the uranium oxides. By the nature of the operations, uranium losses were inevitable in some of the steps, but uranium metal products were obtained. The uranium product from the first
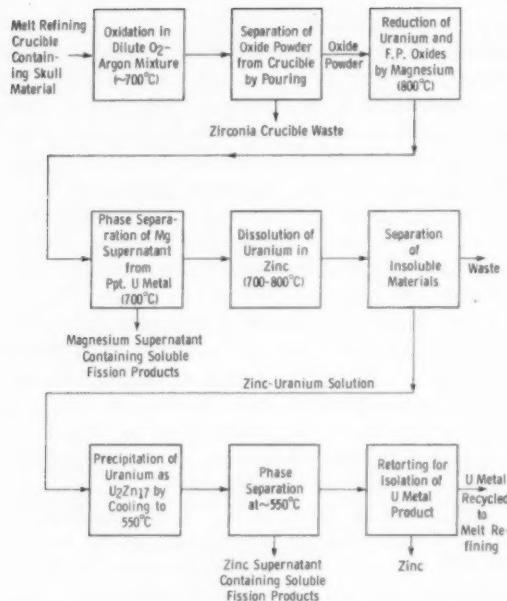
Figure 4 — Liquid-metal process for reclamation of melt-refining skulls.[43]

run was not satisfactorily sintered in the retorting operations, but in the second run a well-sintered uranium metal product was obtained.

Two factors have been found to be important in retorting for production of compact, easily removable uranium product cakes: (1) keeping the uranium precipitated during retorting reduces entrainment and aids the formation of a compact cake, and (2) the use of ceramic or ceramic-coated crucibles facilitates removal of the product.

An interim report has been issued[55] on the separation of U^{233} bred in a thorium blanket from the thorium by a magnesium extraction. Mention of this process, which is based on the solubility of thorium in magnesium and the simultaneous insolubility of uranium, was made in the previous Review.[22] Various methods have been considered and investigated for recovery of thorium. These include distillation, precipitation of thorium as thorium hydride by hydrogen gas, and precipitation of intermetallic thorium-magnesium by cooling. The lowest practicable temperature for this latter operation is 675°C, at which temperature the thorium concentration is still fairly high, 8.1 per cent. This has resulted in a search for alloying elements that will lower the freezing point of the magnesium phase and not undergo hydriding. One candidate is silver, but little experimental work has been done with the silver-magnesium system in this respect. However, the solubility and dissolution rate of thorium in a silver-magnesium eutectic at 800°C are appreciably higher than in magnesium alone at the same temperature.

The best uranium product produced was one having a thorium-to-uranium ratio of 1. The separation of uranium from a liquid-magnesium phase still poses a problem, and both filtration and decantation are being investigated. The decantation methods appeared more promising because of the simpler handling techniques involved. Construction materials still present problems. Austenitic steels show no visible deterioration, but the products have been contaminated to some extent with iron and nickel.

The use of aluminum as a solvent medium is under investigation by the Dow Chemical Company. In a conceptual process, uranium is first dissolved in aluminum and subsequently precipitated as UAl_3, some of the impurities remaining in the aluminum supernatant. After isolation of the UAl_3, it is decomposed by digesting and washing with excess magnesium or zinc. Recent flow-sheet runs using magnesium[56] show that the conversion of UAl_3 to uranium metal was incomplete, a fact attributed to kinetic rather than chemical factors. However, this conversion is the most troublesome aspect of the flow sheet.

Selective oxidation-reduction reactions to effect desirable distribution of elements between molten zinc and a potassium chloride—lithium chloride eutectic salt are being studied at Ames. Zinc chloride has been employed as the oxidant; magnesium as the reductant. Data have been previously reported in these Reviews[57] on the transfer of uranium, thorium, and zirconium. Recent studies[58] with cerium, uranium, and zirconium show that, on incremental addition of zinc chloride, much of the cerium is transferred before transfer of uranium is appreciable and that the transfer of uranium is nearly complete before that of zirconium begins. Addition of magnesium results in successive transfer of zirconium, uranium, and cerium with similar overlaps. Good separations by this procedure are shown to be possible.

The Alloy Reguline Chlorination Oxidation (ARCO) process under development by Phillips Petroleum Co. at the AEC's National Reactor

Testing Station (NRTS) near Idaho Falls, Idaho, consists of dissolution of uranium-zirconium or other uranium alloys in molten lead chloride. The process has possibilities as a head-end step for aqueous processes or may develop into a separate pyrochemical process. As a head-end step for uranium-zirconium alloys, it enables separation of zirconium from the chloride phase containing the uranium by volatilization of zirconium tetrachloride. Subsequently, the uranium-containing chloride phase can be dissolved in aqueous solvents and processed by solvent extraction. Decladding may also be effected by this process. This was demonstrated by decladding a portion of a PWR blanket pin; the liberated uranium oxide pellets floated at the lead—lead chloride interface.[59]

Recent studies have involved recovery of the lead formed in the dissolution reactions as lead chloride for recycle. The chlorination rate of molten lead initially at $510°C$ depends approximately on the chlorine flow rate;[60] for example, an increase in chlorine flow by a factor of 5.3 effected an increase in lead conversion rate by 4.1. At a chlorine rate of 1.05 g/min, the reaction became too rapid and caused the system to reach red heat. Dissolution of lead in nitric acid followed by metathesis of lead nitrate to lead chloride with hydrochloric acid represents the second possible method. No hydrogen is produced during dissolution. At room temperature 92 per cent of the lead is precipitated as pure lead chloride when stoichiometric amounts of reagents are used.[61]

In studies on an advanced ARCO process,[61] involving isolation of uranium by volatilization of the chloride, the effect of chlorine on the volatility of uranium chloride in molten lead chloride was determined. Melts of approximately 10 mole % uranium chloride were prepared by dissolving uranium in lead chloride. Chlorine was added to reconvert the lead to lead chloride. A 40 per cent excess of chlorine volatilized 1.5 per cent of the uranium, whereas an 80-fold excess volatilized 45 per cent. Unless melt characteristics are altered, complete volatilization does not seem practical. Thermal-arrest studies were begun in the uranium-rich portion of the UCl_4-$PbCl_2$ phase diagram.[59]

Development of a coil type liquid-level gauge for molten metals at high temperatures has recently been discussed.[62] These gauges consist of a coil of insulated copper wire covered with two layers of Fiberglas wound on a soft iron core. The level of sodium was determined by measuring the impedance of the coil at a frequency of 1000 cycles/sec and referring these measurements to a set of calibration curves which were determined at several different temperatures for each coil. The impedance or voltage drop across the coil is measured at a constant current of 100 ma.

The primary difficulty with this type of device is the determination of the calibration curves since the coil impedance is not only affected by liquid level but also by temperature, temperature distribution, and geometry of the installation. To eliminate this problem, successive coils were wound and connected to a four-arm bridge circuit. By use of successive coils the sodium level was then definitely known to be somewhere between the bottom of the lower coil of a pair and the top coil above it. This enabled determination of the liquid level to an accuracy of 1 in. The liquid-level gauge can be replaced without opening the liquid-metal system, is adaptable to automatic operation and recording, and will operate continuously at $1000°F$.

Resistance type level transducers have been designed and tested in NaK systems over the temperature range[63] 300 to $1400°F$. A resolution of better than 0.02 in. and reproducibility of better than 1 per cent was achieved. On-off liquid-level probes have also been designed. Sixteen have operated up to 3000 hr in NaK at temperatures up to $1500°F$ without failure. Recommendations are made for design improvements.

Several hundred references to reports and literature relating to liquid-metal technology have been assembled.[64] The MSA Research Corporation also publishes quarterly abstracts of reports relating to liquid-metal technology, the latest[65] being No. 14, for January 1 to March 31, 1960.

Processing of Ceramic Fuels

Simple recovery and refabrication processes for short-cooled, highly irradiated uranium oxide and other ceramic fuels are under development at several sites. Decontamination of fission products is often a secondary consideration, the primary purposes being repair of irradiation damage, re-enrichment, and refabrication.

The "salt cycle" process under development at Hanford involves dissolution of uranium oxide in a sodium chloride—potassium chloride eutectic by the action of chlorine to produce uranyl chloride, which is subsequently reduced electrolytically to uranium dioxide. Construction of a pilot plant designed to produce daily 5 to 10 lb of electrolytic uranium dioxide is nearly complete.[20]

Further electrolysis runs have confirmed that formation of the desirable dendritic uranium dioxide deposits is promoted by keeping the cathode region relatively free of chlorine. The presence of appreciable concentrations of uranyl chloride in the salt also appears to promote recrystallization of the dendritic form into platelet crystals. This apparently can be controlled.

The chemistry of the sodium chloride—potassium chloride and other fused-salt systems is being studied to identify chemical species and decomposition reactions, to develop analytical procedures, and to determine solubilities and dissolution rates of various compounds.[19,20] The solubility of uranium dioxide in the salt phase at 700°C is very low, less than 0.005 per cent, whereas the trioxide and U_3O_8 have solubilities of 7 and 1.3 per cent, respectively. The solution rate of uranium dioxide is also low, whereas uranium trioxide dissolves fairly readily. In the process, uranium dioxide will be converted to U_3O_8 prior to dissolution.

At Atomics International, oxidation-reduction cycles are being investigated for low-decontamination processing of oxide fuels. Fuels may be declad and pulverized by exposure to various partial pressures of oxygen at 600 and 375°C, forming U_3O_8 which is subsequently reduced by hydrogen at 650°C. Some decontamination from cerium, ruthenium, tellurium, iodine, and the rare gases is realized, but the primary goal is re-enrichment and refabrication of fuel shapes.

A two-pronged effort is being followed on this program:[66] (1) process demonstration on a 100-g scale with highly irradiated fuel (several thousand megawatt-days per ton) and (2) process scaleup with simulated high burnup fuel (fissium) to develop engineering methods and equipment. A report describing scaleup studies on a $2\frac{1}{2}$-kg level has recently been issued.[67] The pulverization procedure was found to work equally well for comminution of fissium or uranium dioxide. Both the uranium dioxide

and fissium powders were refabricated into pellets of greater than 90 per cent theoretical density. Pellets of 98 per cent density were prepared from finer powders prepared by additional oxidation-reduction cycles.

An investigation of the kinetics and mechanisms of reactions pertinent to uranium carbide processing is also being carried out at Atomics International. A recent article[68] has discussed the potentialities of uranium carbide as a reactor fuel material. Chemical reactions of uranium carbides have also been discussed.[69]

Homogeneous Reactor Fuel Processing

In the homogeneous reactor concept, fissionable material that is either dissolved or suspended in some fluid medium is circulated through the reactor core. Although the inventories of fuel required are large, the concept does have the potential advantage that a side stream of fuel can be removed and processed on either a continuous or batch basis. The aqueous Homogeneous Reactor Test (HRT) at Oak Ridge is one such reactor, and a chemical processing plant has been constructed as an integral part of the installation.

The primary processing scheme at the HRT is the use of liquid-phase hydroclones for the separation of suspended solids from fuel. During plant operation, solids removal rates continue to be lower than desired,[70] about 1 g/hr. The chemical compositions of the separated solids are monitored routinely and have remained fairly constant through the bulk of operations. Recently, the zirconium content of the solids increased significantly, indicating additional corrosion of the core tank amounting to 1 to 3 kg through the first 1200 hr of Run 21 (reference 70). The average composition is as follows: 50 per cent zirconium, 14 per cent iron, 4.5 per cent chromium, and 2.8 per cent titanium. The ratio of uranium to corrosion product solids ranged from 0.10 to 0.25.

Although the hydroclones are used for the removal of undesired solids from the fuel solution, a means of removing soluble constituents was needed. The accumulation of corrosion-product nickel is the most objectionable of the soluble constituents. It is objectionable for two reasons: (1) it poisons the system, and (2) it is a potential source of fuel-solution insta-

bility. An electrolytic cell has been under development for removal of nickel. The progress of this development has been reported from time to time in these Reviews. Consolidation of this information into a single topical report has been done.[71] Included in the report are the results of testing an HRT prototype electrolytic cell with a mercury cathode and a platinum anode. This was tested for both nickel and manganese removal. Ninety per cent nickel removal and 80 per cent manganese removal were accomplished in 290 amp-hr/liter. The manganese removal required replacement of the liquid-mercury cathode after one-half of the nickel was removed. In the course of this electrolysis, essentially all of the copper was removed and 60 per cent of the uranium was reduced to the four valence state. Further work will be required to improve the radiation stability of the insulators and to reduce the corrosion of the cell.

Corrosion

The selection of construction materials must of necessity be an integral part of all process development. Where processes involve environments that are unusually corrosive, programs have been set up to determine which materials are most promising. In this section an effort is made to consolidate current information on such processes where programs have been established.

Solvent Extraction

Existing AEC production plants for the processing of reactor fuels are of the solvent-extraction type. Some of the newer fuels cannot be dissolved in present equipment or cannot produce feeds that are compatible with existing plants. As a result, several AEC sites are developing head-end procedures for the existing plants to overcome these difficulties.

Hanford will process those power-reactor fuels having a uranium enrichment of less than 5 per cent. As a result of corrosion and process studies, the Zirflex process (ammonium fluoride) and the Sulfex process (sulfuric acid) have been chosen for the decladding of zirconium and stainless-steel fuels, respectively. Vacuum-melted Hastelloy F, although having some limitations, is the preferred construction material. In an effort to overcome the sensi-

tivity of Hastelloy F to intergranular penetration in areas adjacent to welds, Hanford, with the cooperation of BMI, is engaged in an alloy-development program to find a more satisfactory composition. The first 12 experimental alloys prepared by Battelle have been delivered to Hanford and tested. Their compositions, together with that of Hastelloy F, are given in Table IV-9. These alloys were systematically

Table IV-9   COMPOSITION OF 12 EXPERIMENTAL HASTELLOY F TYPE ALLOYS TESTED FOR PROCESS USE AT HANFORD[73]

[Base composition of all alloys, wt.%: 20 to 22 Fe, 45 Ni, 22 Cr, 0.6 Mn, 0.45 Si, and 0.02 C (max.)]

Alloy	Nominal addition, wt.%			
	Mo	Cu	Nb	Ti
1	6	1	2	
2	6	2	2	
3	6			0.5
4	6			1.0
5	3	2		0.5
6	3	2		1.0
7	6	3	2	
8	9	1	2	
9	3	1	2	
10	6	2		
11	6	2		1
12	3	2	2	
Hastelloy F	6		2*	

* Nb plus Ta.

subjected to the Huey test,* and to Sulfex, Zirflex, and Niflex dissolution environments. Tentative conclusions from the studies follow:[72]

1. Unannealed weldments of alloys containing both molybdenum and niobium are subject to sensitization and preferential weld-metal attack by acidic fluoride solutions. Elimination of niobium or substitution of titanium for niobium essentially eliminates both sensitization and weld-metal attack.

2. Corrosion resistance to neutral and acidic fluoride solutions increases with increasing molybdenum content. The effect of molybdenum in the 3 to 9 per cent range on the corrosion resistance to Sulfex decladding solutions is slight.

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*A quality-control test (designated ASTM A262-52T) for determining primarily the susceptibility of corrosion-resistant steels to subsurface attack. The test consists of exposure to boiling 65 per cent nitric acid in five 48-hr periods (fresh acid for each period) under prescribed conditions.

3. Copper improves the corrosion resistance of the alloys to sulfuric acid but has little effect on the resistance to sulfuric acid – stainless steel solutions. In the range of 1 to 2 per cent, copper is slightly detrimental to the resistance of the alloys to acidic fluoride solutions.[72,74]

A second series of 12 experimental alloys is to be made at Battelle.[72,75] Hanford reports that four of these will define more closely the optimum molybdenum content of the basic 45 wt.% nickel – 22 wt.% chromium alloy. The other eight are to provide information on the effects of molybdenum and copper in alloys of greater nickel and chromium content, and of substituting cobalt for part of the nickel. All 12 will be titanium stabilized.[72] Battelle reports that the emphasis on the new list of alloys has been changed; the alloys are to be considered as possible container materials and not as welding alloys for vacuum-melted Hastelloy F. As a result, only self-welded coupons will be used in subsequent corrosion evaluations in boiling Sulfex and Niflex solutions.[75]

The method currently used at the ICPP for the handling of zirconium-matrix fuels is dissolution in hydrofluoric acid in Monel equipment. The process is capable of dissolving these fuels in a homogeneous manner (that is, without leaving a precipitate) only if the fuels have uranium contents of less than about 1 per cent. The procedure developed at Hanford and Oak Ridge for dissolving zirconium-matrix fuels in connection with the power-reactor demonstration program is the Zirflex process. This, too, has a limitation of inability to dissolve higher uranium content fuels homogeneously. Work has been under way on both zirconium process methods to adapt them for homogeneous dissolution of higher uranium content fuels.

One of the methods explored at Idaho to overcome this limitation consists of adding an oxidant such as nitric acid during the dissolution to oxidize the uranium to the more soluble hexavalent state.[76] It was learned that each of four oxidizing agents is capable of producing a homogeneous dissolver solution. These are, together with their concentrations, $1M$ nitric acid, $0.06M$ hydrogen peroxide, $0.06M$ chromic acid, and $0.04M$ potassium permanganate. Corrosion tests were made in which Monel was exposed to the reference dissolver plus each of the oxidants indicated. The reference dis-

solving reagent was $8M$ hydrofluoric acid plus 0.5 g of boron as boric acid per liter. Corrosion rates of 0.02 to 0.05 mil per batch were experienced with the most favorable oxidant used, hydrogen peroxide.[76]

The effort to modify the Zirflex process for higher uranium content zirconium fuels was made at ORNL.[77] The modification was directed to the processing of these fuels at the ICPP in type 309SNb stainless-steel equipment. The modified process for higher uranium content fuels uses $5.4M$ ammonium fluoride – $0.33M$ ammonium nitrate with sufficient $1M$ hydrogen peroxide added continuously during the dissolution to yield a $0.13M$ peroxide in the final solution. Hastelloy F, stainless-steel type 309SNb, Nionel, and Monel were tested in a reference dissolvent with and without $0.03M$ hydrogen peroxide. The reference environment was $6M$ ammonium fluoride – $0.3M$ ammonium nitrate. The presence of peroxide reduced the corrosion of all materials tested except Monel by a factor of 10. Typical corrosion results[77] in the two systems are shown in Table IV-10. It will be noted

Table IV-10   CORROSION RATES IN THE MODIFIED ZIRFLEX PROCESS, REFLUXING $6M$ AMMONIUM FLUORIDE – $0.3M$ AMMONIUM NITRATE, WITH AND WITHOUT $0.03M$ HYDROGEN PEROXIDE[77]

Material	Contact time,* hr	Corrosion rate, mils/month					
		Vapor†		Interface†		Solution†	
Hastelloy F	3	0.07	0.7	7	0.7	7.3	2.3
	6	0.4	0.4	5.3	0.8	7.1	1.7
	9	0.4	0.4	3.8	0.7	5.0	1.4
309SNb	3	1.2	0.7	9.0	1.1	8.7	0.7
	6	0.6	0.1	6.2	0.9	6.1	0.6
	9	0.3	0.1	4.6	1.0	4.6	0.8
Nionel	3	1.4	Gain	9.6	3.3	6.0	0.8
	6	0.5	Gain	7.5	2.0	5.9	1.0
	9	0.2	Gain	6.6	2.1	4.8	1.7
Monel	3	1.6	Gain	6.3	69	9.3	77
	6	2.4	Gain	13.0	73	15.1	91
	9	1.8		10.4		12.4	

*Solution changed each 3 hr.
† The values on the left were obtained without $0.03M$ H_2O_2 in solution, and the values on the right were obtained with $0.03M$ H_2O_2 in solution.

that the corrosion in all cases, except Monel, decreased with time during the short exposure periods used. The results with Monel contrast with the initial corrosion rates observed in refluxing $6M$ ammonium fluoride – $0.003M$ hy-

drogen peroxide, in which Monel corroded at rates of less than 1 mil/month in 24-hr tests.

A room-temperature process for dissolving Zircaloy-2 cladding is being studied.[23] This process seeks to take advantage of low corrosion rates observed for nickel-base alloys and relatively high Zircaloy-2 dissolution rates in nitric acid—hydrofluoric acid solutions at 25 to 50°C. Several corrosion tests were made in a possible dissolution environment of $2M$ hydrofluoric acid—$0.25M$ nitric acid. The alloy tested was one of the 12 experimental alloys having a nominal Hastelloy F composition. Measured rates were less than 1 mil/month.[23]

An investigation was initiated at the ICPP to ascertain whether ceramic alumina might be used as a construction material for service with hydrofluoric—nitric acid solutions.[76,78] The test solution contained $8M$ hydrofluoric acid—$1M$ nitric acid. Preliminary work indicated that the initial corrosion product, presumably aluminum fluoride, tended to prevent attack, although thin porous sections would eventually disintegrate in this solution. Later work, however, showed that even thick sections of the ceramic alumina lost their mechanical strength after extended exposure to the reagent.

Platinum alloys are being explored in a wide variety of process environments in order to find a more suitable "universal" construction material. Iridium and iridium-platinum alloys appear to resist the major chemical reagents of interest for fuel dissolution. Platinum, alloyed with up to 30 per cent iridium, resists attack from all but the most active reagents (fused alkalies), and, even with the most active reagents, the action is not rapid. The presence of large amounts of palladium or rhodium causes the alloy to suffer attack by boiling aqua regia.[76]

The relative corrosion characteristics of welded types 309SNb and 309L stainless steels are being investigated at Hanford. Samples of each type of weldment in the as-welded condition, and heat-treated at 1300, 1500, 1800, 1900, 2000, 2100, and 2150°F were used. These coupons were then exposed to the standard Huey test, boiling $13M$ nitric acid—$0.25M$ hydrofluoric acid, and boiling synthetic Purex 1WW waste solutions. In evaluating the coupons, the areas normally subjected to preferential attack and those adjacent to weld areas were most critically observed.[19,20] In the Huey test, corrosion rates were generally less than 1 mil/

month, and they increased to 3 mils/month over extended periods. In the second environment, corrosion was on the order of 100 mils/month; however, the type 309SNb weld metal was attacked preferentially at rates as high as 1000 mils/month. The type 309L samples showed severe end grain attack. To date, there has been no evidence developed that indicates that type 309L is more satisfactory than type 309SNb for service in nitric acid systems.[19,20]

A type 347 stainless-steel tube bundle in the waste evaporator at the ICPP was recently replaced with a titanium 55A bundle. The former one was removed and submitted for a service test inspection.[76] The unit normally handled a solution containing $1.0M$ to $2.3M$ aluminum nitrate, up to $8.4M$ nitrate ion, $1.3M$ hydrogen ion, low mercury and sodium content, and fission products. The operating steam pressure was 35 psig. Records show that actual time in use was 11 months. Inspection of the unit revealed severe grain-boundary attack on many structural welds. All the tubes suffered end grain attack. The effluent areas of the tubes and the tube sheet suffered the greatest attack. Either temperature gradients or velocity effects could cause accelerated corrosion. Had the unit not been replaced, its early failure would have been considered highly probable.

Fluoride-Volatility Processes

Fluoride-volatility processes are designed to take advantage of the relative volatilities of the fluorides of uranium, plutonium, and fission products. The fused-salt volatility process is directed to the processing of zirconium-matrix fuels and to molten fluoride homogeneous fuels such as that used in the Aircraft Reactor Experiment (ARE). For the latter fuel the molten salt containing uranium tetrafluoride is sparged with elemental fluorine at temperatures in excess of 600°C, thus forming the hexavalent uranium fluoride which is volatilized and removed from the system. For rigid fuels this step is preceded by dissolution in molten salt through which anhydrous hydrogen fluoride is passed.

A pilot plant at ORNL was designed and operated for the recovery of uranium from the molten salt fuel from the ARE experiment. Both process and corrosion data were obtained during this period. A topical report covering these and other operations appeared recently.[79] Cor-

rosion in the volatility pilot plant may be evaluated in four categories: (1) the fluorinator, (2) the molten salt transfer system, (3) the uranium hexafluoride handling system, and (4) the fluorine disposal system. Only the first of these is considered serious for the present scale of operation. The fluorinator was constructed of L nickel and had $\frac{1}{4}$-in.-thick sides and a $\frac{3}{8}$-in.-thick dished bottom. Three distinct regions of corrosive attack occurred in the vessel: (1) vapor, (2) vapor-liquid interface, and (3) molten salt. Corrosion rates were determined by wall-thickness measurements with an ultrasonic device and by metallographic examination of the sectioned vessel. The latter results are shown in Table IV-11. In every

Table IV-11   CORROSION RATES IN THE MARK II
FLUORINATOR AT THE ORNL PILOT PLANT[79]

Region	Corrosion rate, mils/month*	
	Shakedown runs	Av. over final 15 runs
Vapor space	33–46	5–22
Interface	17–23	18–45
Salt wetted area	21–26	41–60

*Based on exposure to molten salt; values include both metal loss and intergranular attack.

region the corrosion mechanism appeared to be a combination of intergranular attack and metal loss by chemical reaction with subsequent dissolution of the nickel fluoride film in molten salt.

A type 347 stainless-steel hold tank contained the reservoir of salt from which each batch was withdrawn. This vessel was exposed to molten salt at 585°C under a nitrogen blanket for 2200 hr. The rate of stainless-steel corrosion by metal dissolution as measured by chemical analysis of the salt batches does not appear to be significant. Corrosion of the Inconel freeze valves and transfer lines was not excessive.

Corrosion of the uranium hexafluoride handling system and of the fluorine disposal system appears to be relatively mild. Both are fabricated from Monel.[79]

In the preceding Review,[22] preliminary corrosion information was presented on a new chemical processing scheme involving NO_2, BrF_3, and HF. A current quarterly report from BNL[40] contains information regarding the corrosion of Inconel, Monel, nickel, and other alloys in NO_2-HF mixtures at temperatures higher

than those previously reported (up to 154°C). Nickel alloys generally are quite satisfactory in the pure environments provided that (1) no complex zirconium salt is present and (2) no direct contact exists between the construction material and the dissolving zirconium.[40]

Pyrometallurgical Processing

Pyrometallurgical processing techniques involve the decontamination of reactor fuels without changing the chemical form. For instance, methods developed at ANL for the processing of EBR-II fuel call for oxidative slagging in an oxide crucible at temperatures well above the uranium melting point. Other techniques include dissolution and crystallization in liquid-metal media. Construction materials for these processes are required to withstand a variety of molten metal environments with an acceptable amount of corrosion.

Corrosion studies involving the resistance of tantalum and tantalum alloys to molten plutonium and plutonium alloy environments at Los Alamos are considered relevant. These studies, although they are not concerned directly with chemical processing, do have significance relative to the techniques employed and in having expected behavior comparable to molten metals of interest. A cooperative alloy development program is presently under way at BMI and Los Alamos.[73-75] The former is producing alloys, and the latter is testing them in molten plutonium and plutonium alloy mixtures. The purposes of this study as stated by Battelle[73] are as follows: (1) to develop binary tantalum alloys for the containment of molten plutonium alloy fuels, (2) to study the effect of radiation on the mechanical properties of tantalum, and (3) phase identification studies for the determination of solid solubility of interstitial impurities over a wide temperature range. The latter objective has resulted from the fact that grain-boundary contaminants are known to have an adverse effect on the corrosion resistance of tantalum in molten plutonium fuel mixtures. These phases are present even in very pure metal, indicating that the solid-solubility limits are exceeded. It is hoped that the identification of these phases can suggest which might be linked with corrosion behavior. Once they are identified, it might be possible to develop metallurgical practices directed specifically toward their elimination. The elements chosen for ad-

dition to tantalum for these studies include tungsten, rhenium, carbon, yttrium, hafnium, zirconium, silicon, and thorium. Some of these alloys have been delivered to Los Alamos and have been tested in tilting furnaces. Early results are as follows: tungsten and rhenium additions in the range of a few per cent showed improved corrosion resistance, whereas carbon was strongly detrimental. The yttrium content of the specimens tested showed less than 0.001 wt.% retained, but the resulting tantalum showed improved performance that suggested a scavenging action.[80]

Instrumentation and Equipment Design

An ultrasonic instrument for measuring the resin level in an ion-exchange column has been developed. The sensing element is adaptable to remote installation and will withstand hot nitric acid solutions in gamma-radiation fields to a total dose of 10^9 r. The problems encountered in development, the limitations, and the capabilities of the instrument are described in a recently issued report.[81] The calibrating procedure, the operating instructions, and notes on circuit operation are also included.

Absorptiometric determination of heavy elements in chemical process streams using a gamma beam is a well established technique. In this method the gamma radiation from a radioactive source passes through a sample; a radiation detector, usually an ionization chamber, measures the unabsorbed radiation. The amount of the absorbed radiation will be a function of the concentration of the heavy element. An extension of this technique by the development of an instrument using an X-ray source for measuring heavy-element concentrations has been reported.[82]

The X-ray instrument worked well with both a d-c and an a-c servoamplifier. Except at low concentrations (less than 5 g/liter), precision measurements of better than 3 per cent of the indicated reading were obtained using aluminum disks to simulate a 1-in.-thick uranium solution. Using the a-c system, a precision of better than $\frac{1}{2}$ per cent of the reading resulted from simulated uranium samples in the 50 to 100 g/liter range. Precision measurements of better than $1\frac{1}{2}$ per cent of the indicated readings were obtained using $1\frac{3}{4}$-in.-

diameter uranium solution samples of 6 to 10 g/liter concentration. With proper system adjustment, a precision of 1 per cent of full scale was obtainable on all ranges. Operation of either system is possible through an additional $\frac{1}{8}$-in.-thick stainless-steel absorber. It is possible that, with proper adjustment, the d-c system with the auxiliary amplifier could operate through much thicker stainless-steel absorbers.

A report on hydraulically driven metal-diaphragm pumps capable of pumping small quantities of highly radioactive, corrosive solutions into high-pressure systems has been recently issued.[83] These pumps must have a long maintenance-free life, be absolutely leak-proof, be resistant to the radioactive and corrosive environment, and be easily replaced by remote methods, when necessary. The report summarizes the development program, the operating experience with the pumps in tests and in reactor service, and the design information derived from the development program. In this program, detailed information has been developed concerning drive systems, diaphragm heads, and check valves, the ultimate objective being the selection of a pumping unit on the basis of a sound knowledge of stresses, materials, configuration, and hydraulics. It has been shown that, with proper design and materials selection, the diaphragm heads and check valves can operate continuously for about two years.

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WASTE DISPOSAL

Annual AEC Report to Congress

The AEC has issued its Annual Report to Congress[1] for 1959. One part of this report has been devoted to the management of radioactive wastes. The following subjects were covered: sources and problems of radioactive wastes, waste management, research on waste disposal, environmental research, licensing, regulation, and inspection. Two appendixes list organizations licensed to dispose of their own waste at sea and firms providing commercial waste-disposal service.

Operating Experience

A survey of a waste-disposal site in the ocean 15 miles off Boston Harbor was completed by the AEC. The site was formerly used for the disposal of packaged low-level radioactive wastes.[2] In the survey, no evidence of radioactivity due to the disposal operations was found. Between 1952 and 1959, Crossroads Marine Disposal Corp. of Boston disposed of a total of 2434 curies of waste at the site. (In August 1959 the company's license was amended to require disposal of wastes further offshore, at a minimum depth of 1000 fathoms.)

A radiological survey of the Clinch River downstream from ORNL was begun by the AEC to determine the dispersion and ultimate fate of radioactive materials released to the river and to evaluate the detailed physical, chemical, and biological phenomena involved.[3]

Reduction to Solids

In recent literature, work is reported on solidification of wastes by adsorption of activity on clay and by high-temperature calcination of waste solutions. A satisfactory method for immobilizing contaminated ion-exchange resins by the use of a mixture of litharge and glycerine as a binder is also reported.[4]

Adsorption on Natural Materials

At Hanford the use of the mineral clinoptilolite for the decontamination of various types of wastes is under continuing investigation.[5-6] For condensate resulting from the self-boiling of wastes in storage tanks, a radiostrontium decontamination factor of 10 to 100 and a radiocesium decontamination factor of 10^3 to 10^4 were achieved with a 22-cm-long column of clinoptilolite. Increasing the length of the column produced no additional strontium removal. Some radiostrontium was removed by passing the solution through a bed of activated carbon, but none of the radiocesium was removed. An aged Redox (high-aluminum salt) waste, diluted 1:20 with distilled water, was passed through four 2-ft clinoptilolite columns in series at a flow rate of 50 gal/(sq ft)(hr). Ninety-eight per cent loading could be attained in the first column before Cs^{137} reached 0.1 maximum permissible concentration (MPC) in the effluent from the third column. The waste used is the supernatant solution from a six-year old Redox tank and its activity is more than 99 per cent Cs^{137}. The cesium from about 50 volumes of the undiluted waste can be loaded on 1 volume of clinoptilolite. Only 0.14 per cent of the cesium was removed by 100 column volumes of water. Less than 25 bed volumes of saturated sodium nitrate solution eluted essentially all of the radiocesium from the bed.

For decladding wastes diluted 1:20 with distilled water, initial data indicated a radiocesium decontamination factor of more than 10^7 for a 240-cm column of clinoptilolite. A diluted

Purex high-level waste was passed through a clinoptilolite column, and the cesium was eluted with 10M ammonium nitrate. Preliminary data indicated a capacity of about 600 column volumes of 20:1 diluted waste.

Calcination

At Hanford, the 8-in.-diameter radiant-heat spray calciner was used successfully for the calcination of Purex process decladding wastes and Darex wastes.[5-8] Darex process waste (nitric acid solution of iron, aluminum, chromium, and nickel) was calcined both "as-received" and after neutralizing with ammonia. The density of the product was 0.81 g/cm^3 for the acidic Darex waste and 1.3 g/cm^3 for the neutralized material. Purex decladding waste was mixed with first-cycle raffinate and calcined with the addition of 125 g of sugar per liter. The product was a fine white powder with a density of 0.65 g/cm^3. An attempt to calcine decladding waste without admixture with first-cycle raffinate was less successful due to the low bulk densities and deliquescence of the products.

Purex process waste contains sulfate in addition to nitrate and metallic ions. Sulfate is troublesome in waste calcination because of severe off-gas handling and corrosion problems during calcination and because of subsequent decomposition during storage, with evolution of noncondensable gases. The volume of noncondensable gases which might be evolved from calcined wastes during storage was determined to be as great as 30 liters/kg. This implies that it is not safe to assume that solid wastes from continuous type calciners can be safely stored unvented and allowed to self-heat to 850°C simply because they have been subjected to this temperature during calcination. Postcalcination heating of spray-calciner powders to 950°C showed that there was a 30 to 40 per cent weight loss. This weight loss was found to be substantially reduced by addition of calcium and even more, by a factor of 10, when 250 g of sugar per liter was added to the waste prior to calcination. The calcium presumably forms thermally stable calcium sulfate, whereas sugar promotes decomposition of most of the sulfate in the spray-calciner itself. High-sulfate Purex waste neutralized with calcium hydroxide instead of caustic was calcined without difficulty to a fine orange-red powder, density 0.7 g/cm^3.

Hanford continued to test its fluid-bed waste calciner unit.[6-8] Various feed-nozzle designs were tested. A simulated high-acid Purex waste and a simulated high-acid Purex waste containing high iron and high sulfate were used as feed solutions. The use of the internal-mixing nozzles (Spraying Systems Company) resulted in severe agglomeration at the nozzle and a rapid buildup in the bed of excessively large particles with a subsequent loss of fluidization. During operation with a modified ANL type nozzle,[5] no feed-nozzle pluggage occurred as a result of nozzle lump formation even though the atomizing air flow rate was reduced. A moderate amount of agglomerate formation in the calcine (1 wt.%) occurred with the feed containing high iron and sulfate. The reduced tendency to lumping was a definite improvement over that of the standard nozzles used so far. With the feed that did not contain high iron and sulfate, performance of the modified ANL feed nozzle was characterized by negligible agglomerate formation and near steady-state particle-size conditions. The atomizing air flow requirements for this nozzle were only 75 per cent of those for the "standard" nozzle. The total off-gas solids entrainment amounted to 1 to 4 wt.% of the product.

In work at the ICPP, laboratory and pilot-plant testing of various components of the Idaho calciner off-gas system has been carried out.[10] Adsorption-desorption cycle runs were made on a silica gel column to evaluate its capacity for adsorbing ruthenium from the calciner off-gas. A trend toward increasing decontamination factors with continued use of the column is indicated from the results. Essentially all of the ruthenium was adsorbed in the first 60 per cent of the column. Washing was only moderately successful in removing the adsorbed ruthenium.

In tests of venturi scrubbing of particles from the off-gas, it was noted that high scrubbing efficiency accompanied high pressure drop across the scrubber. An electrostatic precipitator removed up to 99 per cent of submicron alumina particles. Highest removal efficiencies were obtained at the highest voltages (10,000) and the lowest aerosol velocities (0.88 ft/sec) tested. A total of 1680 hr has been accumulated on the testing of a pulsed blow-back sintered-metal filter system. No apparent loss of filtering effectiveness has been noted.

A countercurrent contactor has been developed and tested for continuous leaching of cal-

cine. Leaching of waste calcine may be required for the following reasons:

1. Removal of long-lived fission products so future ground-water contact would not pick up contamination.

2. Removal of high-heat-producing (short-lived) fission products.

3. Removal of corrosion-producing nitrates.

The heat-liberation rate of an ICPP first-cycle plant waste stored in a 300,000-gal-capacity tank was determined in order to obtain data for the estimation of heat-generation rates of alumina in storage. From measured and calculated values, the heat-generation rate was determined to be 1.96 Btu/(hr)(lb of aluminum oxide).

Separation of Specific Isotopes

The recovery of Cs^{137} from the alkaline supernatant in tank-stored Purex waste is being investigated at Hanford.[8] The supernatant contains some 13 curies of well-aged Cs^{137} per gallon. Two approaches were found technically feasible. One involves the precipitation of cesium with zinc ferrocyanide, and the other, the use of inorganic ion exchangers. Experiments with zinc ferrocyanide were directed toward precipitation of cesium from alkaline solutions containing the concentrations of carbonate and nitrite found in the supernatant. Cesium recoveries ranged from 91 to 98 per cent. Neither carbonate nor nitrite interfered with cesium recovery.

Two absorbers, the mineral clinoptilolite and the synthetic inorganic ion-exchanger Decalso, were treated batchwise with full-strength supernatant. On completion of the loading cycle, the bed was washed exhaustively with water and eluted with $10M$ ammonium nitrate. The loading behavior and the elution behavior of the two absorbents were essentially identical. The Decalso loaded to over 80 curies of cesium per gallon, and over 95 per cent was removed with only four bed volumes of $10M$ ammonium nitrate. Very little cesium was removed by water washing.

Studies at Hanford[7,8] have shown that more than 90 per cent of the ruthenium in a distilled water solution at pH 5 and 8 was removed by the metals iron, aluminum, magnesium, zinc, manganese, and lead. Column experiments with granular lead and magnesium showed lead to be superior for removing ruthenium from $1.0M$ sodium nitrate solutions at pH 12.

Gaseous Wastes

The Harvard University Air Cleaning Laboratory has evaluated the performance of various commercially available filters for NaK fume removal.[11] They concluded from their studies the following:

High-efficiency precleaner and absolute type filters show high efficiency in NaK fume retention but do not have adequate holding capacity. NaK fume removal by dry filtration methods is limited to collector designs which allow fume to disperse throughout the depth of the fiber bed. Deep bed type filters composed of bulk or bonded corrosion-resistant Dynel fibers with diameters in the 10- to 50-μ range provide good holding capacities, efficiencies in excess of 90 per cent, and a moderate final resistance. Bonded fibers are preferable to bulk material since the former have better uniformity in bed structure and minimize channeling of air flow.

Wet collectors, i.e., venturi scrubbers and Peabody scrubbers, may be preferable if large amounts of fumes are present. However, power costs are high for continuous operation, and intermittent use requires maintenance for standby readiness. Electrostatic precipitation appears to be an excellent method for NaK fume removal provided that capital cost is not excessive.

In the event of radioactivity levels presenting handling and cleaning problems, all methods of NaK collection discussed in the report are amenable to remote cleaning. Additional facilities would be required for liquid disposal.

Final Disposal Methods

Sea Disposal

An International Atomic Energy Agency (IAEA) report concludes that nuclear wastes of low- and intermediate-level activity may be safely disposed of in the sea "under controlled and specified conditions."[12] However, the report states that "at present the release into the sea of highly radioactive wastes from irradiated fuel cannot be recommended."

The panel's conclusions and recommendations are based upon the assumption that only those disposal methods should be employed which do

not involve an unacceptable risk of injurious exposure to radiation. In assessing the acceptability of such risks, the panel used the International Commission on Radiological Protection (ICRP) exposure-limit recommendations. The panel did, however, note that its findings "must be subject to continued reevaluation in the light of the rapid accumulation of new data."

The report recommends that all sea disposal operations (with the exception of the disposal of wastes from nuclear shipping) be conducted at designated sites and in conformance with conditions specified for each individual site. The establishment of an IAEA-maintained "international register" of information on all sea disposal sites and operations was suggested.

Open sea conditions (more than 10 miles from shore and 200 fathoms in depth) are regarded by the panel as suitable for the discharge of normal operating waste of presently designed nuclear ships powered by pressurized-water reactors.

Land Disposal

Two interim land burial sites have been established by the AEC for the disposal of solid, packaged radioactive wastes generated by AEC licensees. The sites are located at the Commission's Oak Ridge National Laboratory grounds, Oak Ridge, Tenn., and at the National Reactor Testing Station near Idaho Falls, Idaho.[13] Aspects of waste-disposal licensing are discussed in Section I of this Review.

Rome Symposium

In June 1959, an international symposium on the safety and location of nuclear plants (VI Rassegna Internationale Electronica e Nucleare) was held in Rome, Italy.[14] The proceedings, which include a number of papers dealing with waste disposal, have been published in two volumes. Among the subjects covered are the handling of radioactive solid wastes, the disposal of high-level liquid wastes, the use of ion-exchange methods, and the treatment of plutonium wastes. A list of the titles and authors of these papers follows:

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—The Handling and Disposal of Radioactive Solid Wastes, R. H. Burns (in English).

—Treatment and Final Conditioning of Solid Radioactive Wastes, J. Carré (in French).

—Ultimate Disposal of Liquid Radioactive Wastes, L. P. Hatch (in English).

—Treatment of Radioactive Effluents by a Combined Chemical and Ion-Exchange Process Storage of the Concentrated Sludges, P. Dejonghe and L. Baetsle (in English).

—Effluent Problems of a Plutonium Production Center, R. Galley and J. Cantel (in French).

—Biological Implications of Radioactive Wastes, H. A. Kornberg (in English).

—Treatment of Radioactive Waste Produced by a Naval Nuclear Power Plant, L. Pizzi (in Italian).

—Water Treatment and Safety in Nuclear Installations, D. de LaMorinerie (in French).

—Site Choice Considered in Relation to Problems of Radioactive Effluent Disposal, F. Duhamel (in French).

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PRODUCTION OF URANIUM, THORIUM, PLUTONIUM, AND THEIR COMPOUNDS

Uranium

Uranium Trioxide Production

The feasibility of operating a uranyl nitrate denitration process on a continuous basis has been demonstrated recently at the National Lead Co. of Ohio.[1] This scheme involves the continuous introduction of uranyl nitrate into an agitated pot and simultaneous withdrawal of the oxide product. Descriptions of development work on the continuous pot denitrator have appeared in recent Reviews.[2,3] The continuous pot denitrator has been tested in a plant-scale operation. Production rates equal to those obtained by batchwise operation were obtained without difficulty.

Reactor temperatures lower than those required for batch denitration were found adequate.

A schematic drawing of the continuous denitration pot appears in Fig. 5. Molten uranyl nitrate (70 per cent concentration) at 115°C is fed by gravity to the denitration pot from a storage tank. The feed is introduced into the pot by means of two steam-cooled feed tubes which extend beneath the surface of the orange oxide bed. Temperature of the bed is maintained at $240 \pm 3°C$. The pot is heated by a series of gas burners; the rate of heating is adjusted manually. The bed temperature is maintained at a constant value by adjusting the feed flow rate. Orange oxide leaves the pot through a center overflow port.
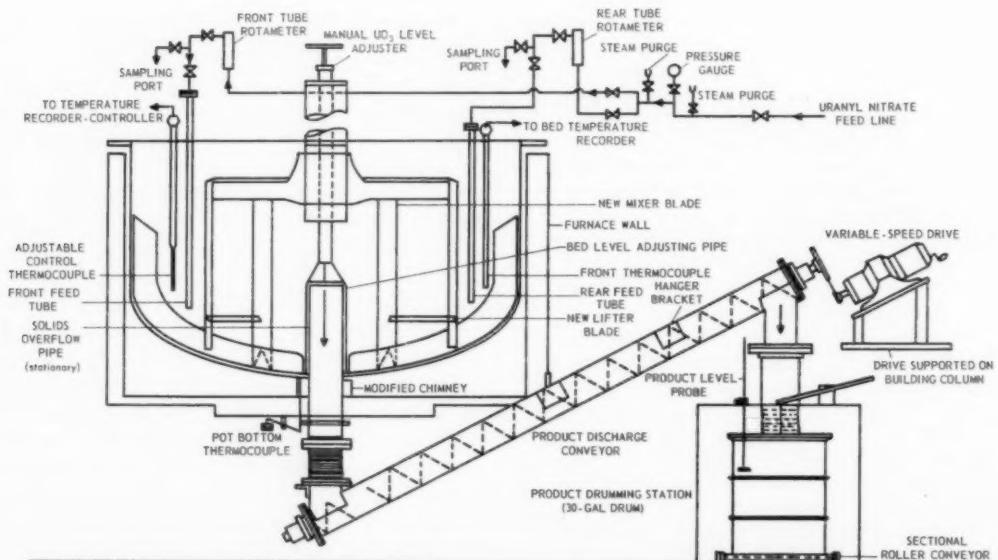
Figure 5 — Continuous denitration pot.[1]

Production rates of 550 lb of uranium trioxide per hour were obtained in preliminary runs. A 50 per cent increase in production rates over batch processing is expected. The product contained 0.42 per cent nitrate, 0.26 per cent water, and 0.16 per cent U_3O_8. The reduction rate of the product from the continuous pot to uranium dioxide is relatively slow compared to material made by batch denitration. The rate may be increased by grinding and sulfonation. Sulfate concentrations of 2500 ppm clearly have a beneficial effect on reduction reactivity but do not seem to affect the hydrofluorination rate. Unground oxide has a particle size too large to be considered acceptable for feed in green-salt manufacture where fluidized-bed reduction reactors are used. Particle comminution tests were performed to ascertain any increase in particle reactivity and applicability to fluid-bed processing. Grinding in a hammer mill to 24 per cent −325 mesh increased uranium trioxide reactivity. The fluid-bed conversion rate to uranium tetrafluoride was variable at a processing rate of 500 lb/hr. The conversion ranged from 86 to 96 per cent uranium tetrafluoride. Grinding to 69 per cent −325 mesh powder produced a material that fluidized satisfactorily and consistently converted to 96 per cent uranium tetrafluoride at a nominal feed rate of 500 lb/hr.

A description of a continuous process for the production of a uniform uranium trioxide powder from uranyl nitrate solution in a fluid-bed reactor has recently been published.[4] Details of the process under development at Mallinckrodt Chemical Works have appeared in a previous Review,[5] and pilot-plant studies are continuing.[6] Work continues on the development of a continuous fluid bed for the production of UO_2 from *unground* granular UO_3 produced in the fluid-bed denitration.[6]

Uranium Dioxide Production

A new process for the production of uranium dioxide from ammonium diuranate has been studied by Eldorado Mining and Refining, Ltd., of Canada.[7] Ammonium diuranate is treated with carbon dioxide, hydrogen, and anthraquinone under 900 to 1000 psi pressure. The uranium is reduced first to U_3O_8 through a uranyl carbonate intermediate. Anthraquinone continuously passes between the reactants and a platinum-coated stainless-steel sheet catalyst. At the catalyst surface the anthraquinone is reduced to hydranthraquinone which reacts with U_3O_8 to form beta-uranium dioxide and finally alpha-uranium dioxide. The reduction may be stopped at any intermediate stage to yield a uranium dioxide of any oxygen-to-uranium ratio desired. Recycling uranium dioxide yields a product with coarser particle size. By varying the carbon dioxide pressure during the reduction, the surface area of the uranium dioxide product may be controlled. The process is said to have the advantages of uniform product surface area, lower pellet sintering temperatures, and lower production costs.

A description of the techniques used in producing uranium dioxide from uranium hexafluoride at the hematite plant of Mallinckrodt Nuclear Corporation appeared recently in an article by Placek and North.[8] Some details of the equipment used in processing various grades of U^{235} enrichment are presented. A general description of the process appeared in a previous Review.[9]

Uranium Tetrafluoride Production

Fluidized-Bed Reactors. Uranium tetrafluoride manufactured from uranyl nitrate solution by use of fluidized solid techniques has been developed on a large scale at the UKAEA Springfields Works.[10] The process conception and the equipment design are similar to those described previously.[5,11] A quadruple effect evaporator is used to remove most of the water from the uranyl nitrate solution before introduction into the fluid-bed calciner. The concentrated uranyl nitrate solution is injected under pressure into the bed of uranium trioxide through a nozzle which projects 9 in. into the bed. A jet of compressed air atomizes the liquid feed. The principle of operation of this denitration unit is similar to that under development at Mallinckrodt, but the productivity per unit of bed volume is much lower for the Springfields denitrator owing to a more dilute feed and a much smaller amount of heater surface area. Both the reduction of the trioxide and subsequent hydrofluorination are performed in batch-operated fluidized beds. Excess hydrogen fluoride is recovered in a distillation column operating about an azeotrope containing 38 per cent hydrogen fluoride in water.

Moving-Bed Reactors. Moving-bed reactors for the production of uranium dioxide and

uranium tetrafluoride have been evaluated on a pilot-plant scale in the United States and Canada.[12] A full-scale plant for the production of nuclear grade uranium tetrafluoride by a moving-bed process has been built and successfully operated at the Eldorado Port Hope refinery. Continuous operation[13] at design capacity began in December 1958. The feed to the reduction reactor is prepared by mixing uranium trioxide powder with water followed by casting, drying, and curing to form hard pellets of hydrated uranium trioxide. This feed-preparation unit has a capacity of 1000 lb of hydrated pellets per hour. The pellets are of a pyramidal diamond shape, $\frac{5}{8}$ in. long, $\frac{3}{8}$ in. wide, and $\frac{3}{16}$ in. deep at the base. The reduction reactor is a 14-in.-diameter vessel, approximately 16 ft high. Design capacity is 270 lb (1 lb-mole) per hour of uranium dioxide. Superheated steam at 315°C is admitted concurrently along with the pellets at the top of the reactor to dehydrate the uranium trioxide. The actual reduction is carried out in the lower portion of the reactor at 540 to 590°C. The reducing gas is dissociated ammonia which is generated by passing anhydrous ammonia over a nickel catalyst at 930°C. A blanketing gas of nitrogen and carbon dioxide is introduced to control the reaction temperature.

Hydrofluorination of uranium dioxide is conducted in a 14-in.-diameter 24-ft-high reactor. Design capacity is 1 lb-mole of uranium tetrafluoride (314 lb) per hour. Hydrofluoric acid vapor at 590°C is fed into the bottom of the reactor. Five vibrators are used to maintain steady flow throughout the reactor. The bed temperature in the main reaction zone is maintained at 540 to 590°C by steam cooling coils and nitrogen blanket gas spargers. Approximately 10 per cent excess hydrofluoric acid is used. Most of the product produced thus far at Port Hope exceeds 99 per cent uranium tetrafluoride with a total metal contamination less than 150 ppm. Uranyl fluoride concentrations less than 1 per cent were consistently obtained.

An innovation of the moving-bed reactor has recently been developed in France at Le Bouchet.[14] Instead of using separate reactors for reduction and hydrofluorination, one reactor in two stages accomplished the same result. Pelletized uranium trioxide enters the top of the two-stage reactor and is reduced in a gas stream of cracked ammonia. The uranium dioxide passes through a conical gas barrier into the lower hydrofluorination stage. Although the uranium tetrafluoride product from the moving-bed reactor is suitable for direct reduction with calcium, it may contain too much oxygen for magnesium reduction. Therefore a horizontal screw hydrofluorinator is incorporated to ensure complete conversion. The fluoride thus obtained is 98 per cent uranium tetrafluoride. Several units of this design are being constructed at Le Bouchet to give an annual production rate of 500 tons.

Uranium-Metal Production

Reduction from Uranium Hexafluoride. As reported in a previous Review,[15] uranium hexafluoride has been experimentally reduced directly to uranium metal by a vapor-phase reaction with sodium metal. A recent development is the reduction with sodium under positive pressure.[16] Volatile uranium hexafluoride is transferred into a nickel container in the reduction furnace where the gas is reduced by sodium in the presence of sodium chloride which forms a low-melting mixture (650°C) with the sodium fluoride by-product. Difficulty was experienced in producing a compact uranium-metal sponge. Under certain conditions of temperature, the metal forms by vapor-phase reaction, whereas in other cases the metal is in the form of a powder suspended in the by-product salts. In an attempt to produce consolidated metal, the use of various halide fluxes was tried without complete success. The uranium produced during a 650°C reduction with LiCl-KCl flux was found to be only partially reduced.

Uranium metal has been produced by a two-step reduction process using calcium metal.[16] The uranium hexafluoride is partially reduced at 900°C; then the temperature is increased to 1200°C to consolidate the metal and complete the reduction. This two-step reduction procedure aids in minimizing the corrosion problems associated with uranium hexafluoride at the high temperature of the final reduction.

Reduction from Uranium Dioxide. Piper and Leifield[17] suggest that the economics of uranium-metal production indicate that an electrolytic process designed to replace the currently used magnesium reduction of uranium tetrafluoride must yield massive uranium metal directly from a uranium oxide rather than from a halide. Recent work has demonstrated the feasibility of producing massive molten uranium by fused-

salt electrolysis using a consumable uranium dioxide – carbon anode. A similar process reported previously[9] was complicated by the low solubility of uranium dioxide in the electrolyte. The oxides readily settled from the electrolyte, forming a sludge which interfered with coalescence of the metal. Metal shot was generally the major product of the process. The problem involving the low solubility of uranium dioxide in the electrolyte made it necessary to exclude the oxides from the cathode area of the cell by the use of a consumable anode.

The process is similar to the Hall process for aluminum except for the fact that uranium dioxide is only slightly soluble in the electrolyte and uranium exhibits several valence states in the fused salts. The formation of U^{+4} at the anode and U^{+3} at the cathode probably is the reason for the low (39 per cent) current efficiency obtained in preliminary runs. Two electrolyte compositions (65 per cent $BaF_2 - 10$ per cent $LiF_2 - 25$ per cent UF_4 and 45 per cent $BaF_2 - 15$ per cent $MgF_2 - 40$ per cent UF_4) have been found workable, but no comparative evaluations have been made.

The consumable anodes were prepared by dissolving coal tar pitch in trichloroethylene, adding uranium dioxide and carbon black, and then evaporating the trichloroethylene to give a powder. The powder was pressed at 2000 psi and heated slowly to 1200°C for 3 hr. The anodes contained 2 moles of carbon per mole of uranium dioxide. Graphite was used as the cathode.

Powdered electrolyte was placed in a 4-in.-diameter graphite crucible contained in a 7-in.-diameter quartz envelope. The crucible and electrolyte were outgassed under vacuum at about 700°C, and then the system was filled with helium and heated to about 1050°C. Preelectrolysis with reversed polarity was used at this temperature to remove residual oxides from the electrolyte. After preelectrolysis the system was heated to the operating temperature of 1150°C. Current density at the anode and cathode for a typical run was 1 and 15 amp/cm^2, respectively. A total current of 428 amp-hr at 30 per cent efficiency was used to produce 370 g of metal. Owing to high cathode current density, some metallic barium was formed during the runs. Therefore the reduction efficiency was slightly less than 100 per cent. High-quality metal has been produced in most runs; only

160 ppm carbon was detected in the massive uranium.

Thorium

Preparation of Thorium Tetrachloride and Reduction to Metal

Recently, the U. S. Bureau of Mines initiated the development of a process for the production of thorium metal from thorium tetrachloride.[16] Since the objective of the process is primarily the preparation of low-oxygen-content metal, considerable concern was placed on the production of pure thorium tetrachloride.

Thorium oxide, resulting from the partial calcination of the oxalate, is contacted with 100 per cent excess carbon tetrachloride vapor at 575°C for 24 hr. The process conditions were established in a 5-in.-diameter by 3-ft quartz chlorinator using 10-kg charges. The chlorinator was designed so that the carbon tetrachloride diluted with argon passed over a static bed of oxide. Both the carbon tetrachloride feed rate and furnace temperature were critical. Too high a feed rate during the initial stages of the reaction results in excessive dust losses of thorium oxide. Furnace temperatures in excess of 600°C produce sintering of thorium tetrachloride, making unloading of the chlorinator difficult. Temperatures below 550°C cause the reaction to proceed very slowly. Conversions of approximately 90 per cent were obtained.

The crude thorium tetrachloride is purified by distillation under a pressure of 300 μ Hg at 900°C. The chloride is charged into a nickel crucible placed in the bottom of a 12-in.-diameter stainless-steel retort. The thorium tetrachloride distillate is collected in the upper cool zone on a tubular nickel liner. A 24-hr distillation cycle effected complete volatilization of the chloride on a 38-kg batch. Entrainment of thorium oxide in the vapors is minimized by employing a system of nickel baffles. Nevertheless, a second distillation at a lower temperature is necessary to ensure an oxide-free product.

Several alternate methods for producing thorium tetrachloride are being considered to increase the product quality and the scale of operation. A fluidized-bed chlorinator was tested, but, because of the small particle size of the thorium oxides, it was impossible to maintain a fluidized bed. Varying calcination conditions

to produce coarser particles from thorium oxalate were not successful; nodulization of thorium oxalate was equally unsuccessful. Chlorination of a suspension of thorium oxide in a fused-salt bath to obtain an oxygen-free product is being investigated.

The reduction of thorium tetrachloride with metallic sodium is conducted in a closed retort. The required amount of molten "reactor grade" sodium (approximately 30 per cent excess) is measured into the reduction crucible. After the metal has solidified, the charge of purified thorium tetrachloride is added. The crucible is covered with a thin sheet of magnesium to protect the contents from air during transfer to the retort furnace. In the furnace the crucible is placed under 12 psig of argon pressure. The reduction reaction is initiated at 220°C and completed by raising the temperature to 800°C for 4 hr. The excess sodium and sodium chloride are distilled from the thorium by heating at 900°C under high vacuum. Yields of sponge metal from four runs ranged from 75 to 95 per cent.

The remelted ingots were of variable quality. There was evidence of internal flaws, and one ingot failed after only 25 per cent reduction in area. However, one ingot showed a Brinell (500 kg) hardness of 35 before annealing. Oxygen content of remelted metal was approximately 800 ppm.

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